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A standardized test was established to evaluate the reactivity of the limestones. The following variables are of importance in evaluating limestones for coal mine water neutralization: (a) particle size, (b) Ca and Mg content, and (c) surface area.

Ferrous iron oxidation has been accomplished with both synthetic and actual coal mine water at low pH in the presence of coal-derived activated carbon.

Electrophoretic mobility studies on precipitates obtained by both lime and limestone neutralization of coal mine water yielded information which can be applied for more effective sludge removal.

Magnetic sludges were prepared using two different iron-bearing waters. The conversion of precipitates to a magnetic form results in significant reductions in settled sludge volumes as well as increases in solids content, compared to the initially formed sludge obtained by lime neutralization alone.

Data obtained in these studies indicate that the limestone process offers considerable promise for an improved lower cost method for treating several types of coal mine waters.

Abstractor

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Studies on Limestone Treatment of Acid Mine Drainage

Optimization and Development of Improved Chemical Techniques for the Treatment of Coal Mine Drainage

by

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania 15146

for the

COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF MINES AND MINERAL INDUSTRIES

and

THE FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

DEPARTMENT OF THE INTERIOR

Program Number
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January 1970

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ABSTRACT

Four actual coal mine waters have been neutralized with limestone both on a batch scale and by utilizing a continuous flow apparatus. Variations in treatment procedure were necessary depending on the characteristics of the individual waters.

A standardized test was established to evaluate the reactivity of the limestones. The following variables are of importance in evaluating limestones for coal mine water neutralization: (a) particle size, (b) Ca and Mg content, and (c) surface area.

Ferrous iron oxidation has been accomplished with both synthetic and actual coal mine water at low pH in the presence of coal-derived activated carbon.

Electrophoretic mobility studies on precipitates obtained by both lime and limestone neutralization of coal mine water yielded information which can be applied for more effective sludge removal.

Magnetic sludges were prepared using two different iron-bearing waters. The conversion of precipitates to a magnetic form results in significant reductions in settled sludge volumes as well as increases in solids content, compared to the initially formed sludge obtained by lime neutralization alone.

Data obtained in these studies indicate that the limestone process offers considerable promise for an improved lower cost method for treating several types of coal mine waters.

This report was submitted by Bituminous Coal Research, Inc., in fulfillment of a project FWPCA Grant No. 63-01-68, among the Federal Water Pollution Control Administration, the Pennsylvania Coal Research Board, the United Mine Workers of America, and Bituminous Coal Research, Inc.

Key Words

Coal Mine Drainage
Neutralization
Limestone
Oxidation
Ferrous Iron
Carbon Catalyst
Sludge
Magnetic Sludge
Coagulation
Waste Water

CONTENTS

Abstract

Page

Section 1 Conclusions and Recommendations........................ 1

Section 2 Introduction.. 3

Section 3 Experimental.. 9

Section 4 Discussion.. 23

Section 5 References.. 95

Abstract Cards.. 97

FIGURES

Figure		Page
1	Flow Diagram of Conceptual Limestone Treatment Process	5
2	Apparatus for Neutralization of Synthetic and Actual Coal Mine Waters	11
3	Apparatus for Ferrous Iron Oxidation in the Presence of Coal-Derived Carbons	15
4	Continuous Flow Test Apparatus	19
5	General View of Continuous Flow System	20
6	Neutralization of Synthetic Coal Mine Water with No. 1809 Limestone	31
7	Neutralization of Synthetic Coal Mine Water with No. 1337 Limestone	32
8	Effect of Group A Limestones on Synthetic Coal Mine Water	36
9	Effect of Group B Limestones on Synthetic Coal Mine Water	37
10	Effect of Group C Limestones on Synthetic Coal Mine Water	38
11	Effect of Limestone No. 1809 on Synthetic Coal Mine Water	39
12	Model Curve for Judging Effectiveness of Limestones	47
13	Neutralization of South Greensburg Coal Mine Drainage - Effect of Amount of No. 1809 Limestone on Fe^{2+}	49
14	Neutralization of Keystone Coal Mine Drainage with No. 1809 Limestone - Effect of Aeration on Fe^{2+}	50
15	Neutralization of Keystone Coal Mine Drainage with No. 1809 Limestone - Effect of Aeration on pH	51

FIGURES (continued)

Figure		Page
16	Effect of Activated Carbon on Ferrous Iron Oxidation Tarrs Coal Mine Discharge........................	64
17	Effect of Coagulant Aids on Zeta Potential...........	67
18	Effect of Ludox HS-40, Ludox AS, and Solution No. 24 on Zeta Potential of $Fe(OH)_2$........................	69
19	Effect of $Na_4P_2O_7$, Calgon C-55, and Calgon 37 on Zeta Potential of $Fe(OH)_2$........................	70
20	Effect of Lomar D, Primafloc A-10, Purifloc A-21, and Calgon 240 on Zeta Potential of $Fe(OH)_2$........	72
21	Effect of Poly-Floc 1130 on Zeta Potential of $Fe(OH)_2$..	73
22	Effect of M and D Clay, "Red Dog," and Fly Ash on Zeta Potential of $Fe(OH)_2$.......................	74
23	Effect of Calgon 240, and Calgon 240 and Fly Ash on Zeta Potential of $Fe(OH)_2$.......................	75
24	Effect of Fly Ash and Calgon 240, "Red Dog" and Calgon 240, and M and D Clay and Calgon 240 on Zeta Potential of $Fe(OH)_2$......................	76
25	Effect of Treatment with Fly Ash and Calgon 240 on Settling of $Fe(OH)_2$ Sludge.....................	78
26	Effect of Poly-Floc 1130, Calgon C-55, Primafloc A-16 and Solution No. 24 on Zeta Potential of $Fe(OH)_3$...	84
27	Effect of Purifloc A-21, Ludox AS, and Lomar D on Zeta Potential of $Fe(OH)_3$.......................	85
28	Effect of Calgon 240, Ludox HS-40, and Calgon 37 on Zeta Potential of $Fe(OH)_3$......................	86
29	Effect of $Na_4P_2O_7$ on Zeta Potential of $Fe(OH)_3$.......	87

TABLES

Table		Page
1	Analyses of Three General Categories of Coal Mine Water Selected for Study	24
2	Limestones Selected for Study	25
3	Analyses of Thirteen Limestones Originally Selected for Study - Case I through Case IV	26
4	Analyses of Fourteen Limestones Selected for Study - Case V	27
5	X-ray Analyses of Fourteen Limestones	29
6	Density and Surface Area of Fourteen Limestones	30
7	Effect of Particle Size of Limestones on pH of Synthetic Coal Mine Water - Case I	33
8	Effect of Magnesium Content of Limestone on pH, One Hour After Neutralization and Oxidation - Case I	35
9	"Efficiency" of Limestones - Case II	40
10	Mathematical Relationships Considered in Evaluating Limestones - Case II	42
11	"Efficiency" of Limestones - Case III	43
12	"Efficiency" of Limestones - Case IV	44
13	"Efficiency" of Limestones - Case V	45
14	Batch-scale Limestone Neutralization of South Greensburg Coal Mine Drainage	52
15	Batch-scale Limestone Neutralization of Keystone Coal Mine Drainage	53
16	Batch-scale Limestone Neutralization of Tarrs Coal Mine Drainage	54
17	Batch-scale Limestone Neutralization of Thorn Run Coal Mine Drainage	55

TABLES (continued)

Table **Page**

18 Evaluation of Prepared Carbon Catalysts for Fe^{2+} Oxidation.................................... 58

19 Evaluation of Life of a Prepared Activated Carbon Catalyst.................................... 59

20 Evaluation of Commercially Available Activated Carbons as Catalysts for Fe^{2+} Oxidation.................... 61

21 Evaluation of Life of a Commercially Available Activated Carbon Catalyst.......................... 62

22 Effect of Materials Other than Carbon on Ferrous Iron Oxidation.................................... 65

23 Effect of Coagulant Aids on $Fe(OH)_2$.................. 68

24 Effect of Coagulant Aids on $Fe(OH)_2$ and $Fe(OH)_3$....... 88

25 Froth Flotation Tests................................ 89

CONCLUSIONS AND RECOMMENDATIONS

Based on the experimental data obtained in this study, we conclude the following:

Coal mine water can be neutralized with limestone. Variations in treatment procedures for coal mine water are necessary depending on characteristics of the individual waters.

The limestone process for treating coal mine water involves essentially the same unit operations as the lime neutralization process for coal mine water. A typical sequence of unit operations is: (a) holding, (b) adding the neutralizing agent and mixing, (c) aerating, and (d) sludge settling and disposal.

A method has been established to evaluate the effectiveness of individual limestones as neutralizing agents for coal mine water. Evaluation of 14 limestones utilized in this research program has established the properties of these stones which are responsible for their effectiveness as neutralizing agents. The criteria for effective limestones are: (a) minimum particle size, preferably minus 325 mesh (less than 44 microns), (b) relatively high calcium content, approaching pure $CaCO_3$, (c) relatively low magnesium content, thus eliminating dolomites, $CaMg(CO_3)_2$, and magnesites, $MgCO_3$, and (d) relatively high specific surface area.

The rate of ferrous iron oxidation in actual coal mine water can be increased by aeration in the presence of coal-derived activated carbon. None of the other materials tested was found to be as effective.

As indicated by electrophoretic mobility measurements, the rate of settling of ferrous hydroxide formed by lime neutralization of synthetic coal mine water can be increased by the addition of coagulant aids.

Magnetic sludges can be obtained by controlled, partial oxidation of an alkaline (pH 8) suspension of ferrous hydroxide prepared by the addition of lime to coal mine water having a relatively high ferrous/ferric iron ratio, and an aluminum/total iron mole ratio less than 0.12. The conversion to a magnetic sludge proceeds at a satisfactory rate at temperatures of 80 C or above. Concentration of the raw sludge, by means such as gravity separation and/or centrifugation, is desirable to minimize the volume of material that requires heating.

Aluminum, in an Al/Fe mole ratio of greater than 0.12, interferes strongly with the formation of magnetic sludges. When aluminum is present in amounts below this mole ratio, magnetic sludge can be obtained, but it is lighter in color, more gelatinous, and bulkier than magnetic sludges prepared in the absence of aluminum.

Conversion of ferrous hydroxide precipitated from actual coal mine water to a magnetic form results in at least a five-fold reduction in settled sludge volume and in a six-fold increase in solids content as compared to sludges formed by lime neutralization alone.

It is recommended that the following work be conducted to further optimize the limestone process:

Further development of information on the limestone process utilizing the continuous flow system. Additional data are needed on: (a) the effect of excess limestone, similar to that from studies already carried out on batch scale, (b) the effect of sludge recirculation, including volume of sludge, retention times, and the point of addition, and (c) the effect of coagulant aids on sludge settling.

Further examination of properties of various limestones, such as surface area and reactivity toward synthetic and actual coal mine water, to develop a method for selecting the most effective limestones. These examinations should be directed toward establishing the order of importance of those properties responsible for the effectiveness of limestone as a neutralizing agent for coal mine water.

Further development of the limestone process by operation of onsite research unit(s) based on results from laboratory tests. Engineering evaluations would be made of both portable and stationary field research unit(s). In addition to costs, the number and location of discharges to be treated, the rate of flow, the number of limestones to be utilized in treatment tests, and other process variables would be subjects for consideration. Based on data from the field research unit(s), a full-scale treatment plant would be designed and evaluated. Engineering drawings of any major items of specialized equipment should be included in the evaluation together with cost estimates.

Final development of the process for industrial use by construction and operation of a full-scale treatment plant based on data from the field research unit(s).

It is recommended that the conversion to a magnetic form of ferrous hydroxide sludges obtained by lime neutralization of coal mine water be explored further as a means of producing more dense sludges, improving settling rates, facilitating sludge handling, and increasing plant capacity.

It is further recommended that additional research be conducted on optimizing the oxidation of ferrous iron in mine drainage by activated carbon.

INTRODUCTION

This is the final and summary report on the Pennsylvania Coal Research Board Project CR-75 activated July 1, 1967, with financial support from the United Mine Workers of America, the Pennsylvania Coal Research Board, and Bituminous Coal Research, Inc., and expanded February 7, 1968, with additional financial support for the program through Grant WPRD 63-01-68 to the Commonwealth of Pennsylvania by the Federal Water Pollution Control Administration.

Work on the project was conducted according to the BCR Research Proposal submitted to the Pennsylvania Coal Research Board on December 20, 1966, and as revised in BCR Research Program Proposal RPP-141R2 dated June 12, 1967. In regularly scheduled meetings between the sponsors and the project personnel during the course of the program, the various facets of the program were clarified and work areas more clearly defined. The experimental work was conducted during the period July 1, 1967 to June 30, 1969.

Objectives

The objective of the overall long-range program, is to design and develop to pilot-plant stage an improved process for the control and prevention of pollution of waters by drainage from coal mines, conducting laboratory studies to obtain needed design data.

The objectives of the studies conducted in the period covered by this report were: (a) to improve and optimize the chemical techniques involved in the treatment of coal mine drainage with emphasis placed on limestone neutralization processes, and (b) to further develop, using laboratory pilot scale equipment, the most promising system as judged on the basis of engineering evaluations.

Nature and Scope of the Problem

Acid mine drainage results from the dissolution of oxidation products of pyrite in normally neutral to mildly alkaline ground water. The oxidation of pyrite occurs by exposure to air and water of pyritic materials associated with the coal seam. Acid drainage seriously pollutes some 5,700 miles of the 10,500 miles of streams affected by all forms of mine drainage and represents a significant environmental problem in portions of the Appalachian Region.(1) Inactive sources contribute 78 percent of the acid and active sources 22 percent.(2)

Lime neutralization treatment in conjunction with aeration and settling ponds is the process most generally used or considered for use in treating coal mine drainage. For example, it has been stated that of 252 mine drainage locations requiring treatment facilities in the state of Pennsylvania, 243 are using a lime neutralization treatment.

The claimed advantages of limestone neutralization over lime neutralization are: (a) lower costs for chemical reagent, (b) decreased hazard to the operator handling a less reactive reagent, (c) little or no harmful effect on streams and stream life from an accidental overtreatment, and (d) potential for decreased sludge volume by an increased solids content in sludge.

Two recent reports (3,4) of limestone neutralization studies describe treatment of coal mine water containing iron principally in the ferric state, Fe^{3+}. A greater problem exists in the treatment of coal mine water containing iron principally in the ferrous state, Fe^{2+}. Oxidation of the ferrous iron, Fe^{2+}, whether induced or natural, and subsequent hydrolysis leads to the production of more free acid, H^+. This can be represented by the following reaction.

$$Fe^{2+} + O_2 + H_2O \rightarrow Fe(OH)_3 + H^+$$

It is significant that in the formation of a ferric precipitate, which can be a chemical form other than $Fe(OH)_3$, the overall reaction includes the production of an excess of H^+ thus leading to an acidic condition requiring further neutralization.

While considerable work has been done in this country and abroad on the treatment of coal mine drainage with lime and limestone (5,6,7,8), many gaps exist in the data. Because of this lack of information, diverse opinions of the applicability of lime and limestone neutralization have been held by workers in the field (7,9,10). Little systematic research has been conducted to resolve the differences in results achieved. The present program of laboratory investigation was designed to resolve some of these differences by exploring various facets of the neutralization process and to arrive at a promising system for coal mine drainage neutralization.

Approach to the Problem and Research Procedure

The neutralization of coal mine drainage entails a series of individual unit operations namely, (a) holding, (b) adding and mixing of the neutralizing agent, (c) aeration, and (d) solids separation and disposal. One concept of the limestone treatment process is given in Figure 1.

A study of the individual factors affecting each of the unit operations was undertaken to optimize the overall neutralization process.

Assessment of Coal Mine Water Composition

Coal mine water is, by its very nature, a variable entity. Chemical composition and flow rate from a single discharge varies depending on pumping operations, path through the mine, amount of rainfall, and temperature. Even more variation is found in discharges from different locations.

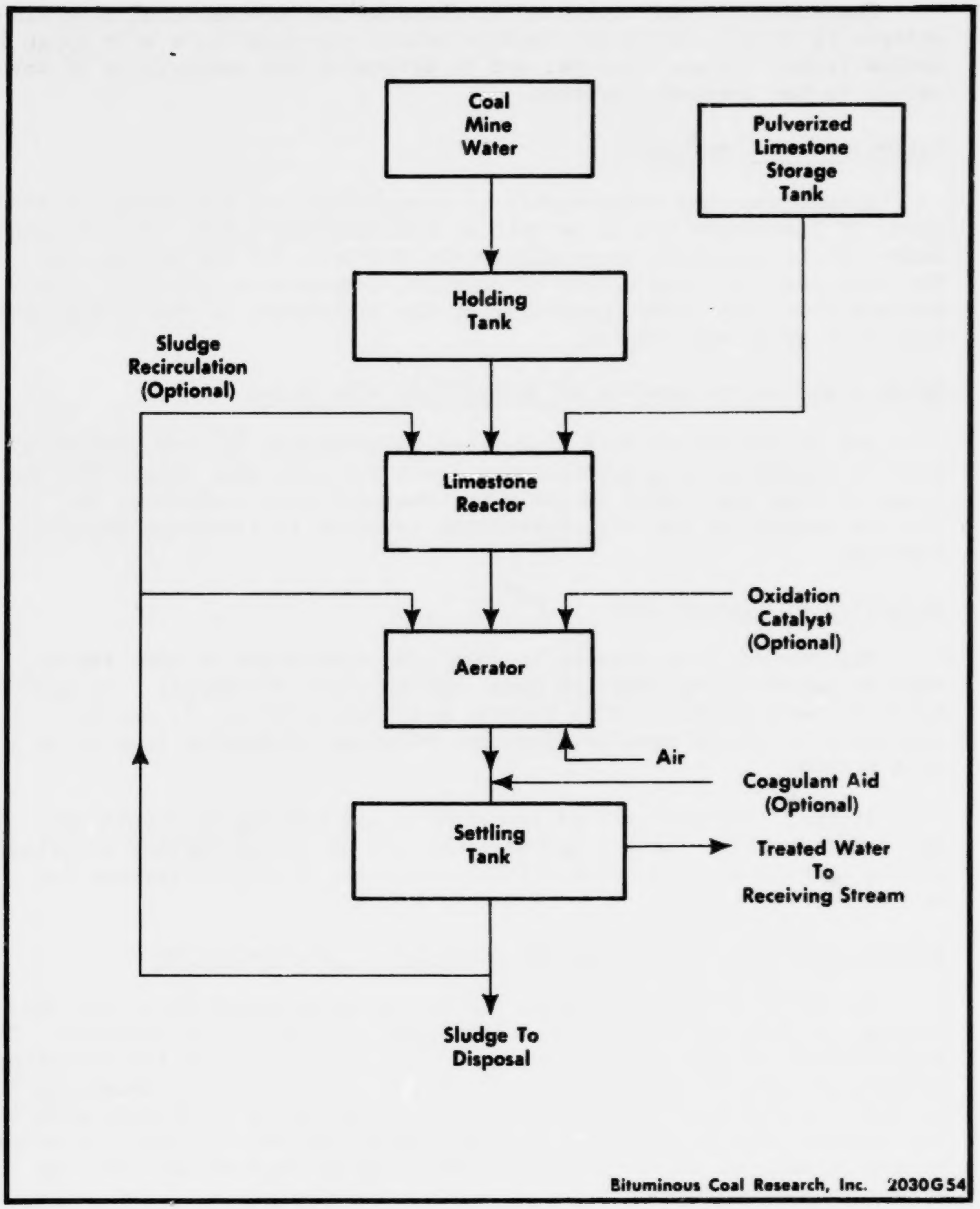
Coal Mine Water
Pulverized Limestone Storage Tank
Holding Tank
Sludge Recirculation (Optional)
Limestone Reactor
Oxidation Catalyst (Optional)
Aerator
Air
Coagulant Aid (Optional)
Settling Tank
Treated Water To Receiving Stream
Sludge To Disposal
Bituminous Coal Research, Inc. 2030G54

Figure 1. Flow Diagram of Conceptual Limestone Treatment Process

Therefore, it was necessary to characterize several coal mine discharges in detail, to select certain waters representing a wide range in compositional characteristics, and to determine the amenability of these waters to the treatment process.

Evaluation of Limestone

Limestones vary considerably in composition and structure. Therefore, if limestones are to be used as neutralizing agents for coal mine water, it is necessary to establish the criteria for evaluating them for this purpose. The effect of chemical composition, particle size, surface area, and other properties of the limestones on reactivity with coal mine water was studied.

Batch-scale Neutralization of Actual Coal Mine Water

The objectives of this study were to establish (a) the effectiveness of limestone as a neutralizing agent for coal mine water, (b) the types of coal mine water amenable to treatment with limestone, and (c) the techniques and unit operations involved in limestone neutralization.

Oxidation of Ferrous Iron

The ferrous iron present in some coal mine water is more resistant to oxidation by aeration than that in other discharges. To promote the neutralization with limestone in such a water, it may be necessary to find a catalyst for the oxidation of ferrous iron in an acid medium.

Initial studies involved preparation and testing of a catalyst derived from coal. Later, emphasis was placed on the further investigation of coal-derived, commercially available activated carbons for use as catalysts.

Non-oxidative Neutralization and Addition of Coagulant Aids

As far as is known, direct, non-oxidative neutralization for the removal of iron has neither been evaluated nor applied in practice. The availability of such a technique would eliminate the need for oxidation of ferrous iron to ferric iron. Studies were conducted to determine the extent to which iron could be precipitated as ferrous hydroxide with lime and removed without oxidation of the iron to the ferric state. Studies were also made on addition of coagulant aids to improve the settling characteristics of sludges.

Magnetic Sludge Studies

Previous work at BCR and elsewhere has confirmed that a magnetic sludge may form during lime neutralization of coal mine water. A sludge of this type could be more easily removed by commercially available wet or dry magnetic separators. One objective of the present study was to explore the conditions under which magnetic sludge forms. A sludge of this type would be denser and settle faster than the sludge usually formed by lime or limestone neutralization.

Miscellaneous Studies

Areas explored in miscellaneous studies were: (a) the effect of coagulant aids on the $Fe(OH)_3$ sludge that will be formed in a limestone neutralization process, (b) flotation, as a technique to separate the sludge from the treated water, (c) use of a calcium ion electrode to detect changes in concentration (activity) of Ca^{2+} during neutralization, and (d) activities on ASTM Committee D-19 on water, related to the analysis of coal mine water.

Continuous Flow Tests

A small laboratory pilot plant was utilized to examine the limestone treatment process for coal mine water under flow conditions which approximate actual treatment plant operations more closely than batch tests.

Process Evaluations

Near the end of this present study, the overall technical and economic feasibility of chemical techniques developed during the course of the program, and the merit of further development of these techniques on a laboratory-scale were considered. Data obtained from the laboratory studies were used for process engineering evaluations.

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EXPERIMENTAL

Apparatus and general procedure for conducting experiments are described below in the various categories: (a) assessment of coal mine water composition, (b) evaluation of limestones, (c) batch-scale neutralization of actual coal mine water, (d) oxidation of ferrous iron, (e) non-oxidative neutralization and addition of coagulant aids, (f) magnetic sludge studies, (g) miscellaneous studies, (h) continuous flow tests, and (i) process evaluation. (See schedule of work as given in Figure 2 above).

Assessment of Coal Mine Water Composition

After examination of a number of coal mine water discharges in the vicinity of the BCR laboratories, four were selected for study on this program. These discharges are classified into three categories: (a) ferrous iron water containing little or no aluminum, (b) ferrous iron water containing a substantial amount of aluminum, and (c) ferric iron water.

Samples were analyzed routinely for: (a) ferrous iron colorimetrically using the o-phenanthroline method, (b) cations, Si, Al, Fe, Ca, Mg, Mn, and Na by emission spectrographic techniques, (c) acidity by adding hydrogen peroxide, boiling, cooling to room temperature, and titrating to pH 8.2, and (d) pH.

Evaluation of Limestones

The reactivity of 14 selected limestones was evaluated by consideration of (a) their physical and chemical properties, and (b) their effectiveness in neutralizing synthetic coal mine water.

Chemical Properties of the Limestones

The chemical composition of the individual limestones was determined by conventional emission spectrographic techniques using a Jarrell-Ash[1] Model 78-000 1.5 meter Wadsworth grating spectrograph. Structure was determined by x-ray diffraction analyses utilizing a Picker Nuclear powder diffraction unit.

Physical Properties of the Limestones

Densities of the 14 limestones were determined with a Beckman air pycnometer. Surface areas were measured by the standard BET

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[1] Mention of commercial products throughout this report does not imply endorsement by the Federal Water Pollution Control Administration.

(Brunauer, Emmett, and Teller) technique using nitrogen as the adsorbate at liquid nitrogen temperatures or by a modified BET technique using a Micromeritics Model 2200 surface area analyzer.

Neutralization Reactions

In five series of neutralization tests (Cases I-V) the reactivity of the limestones toward synthetic coal mine water was observed by varying the amount of limestone, the amount and type of oxidant, and the time at which the oxidant was added.

The general procedure for conducting the neutralization reactions follows:

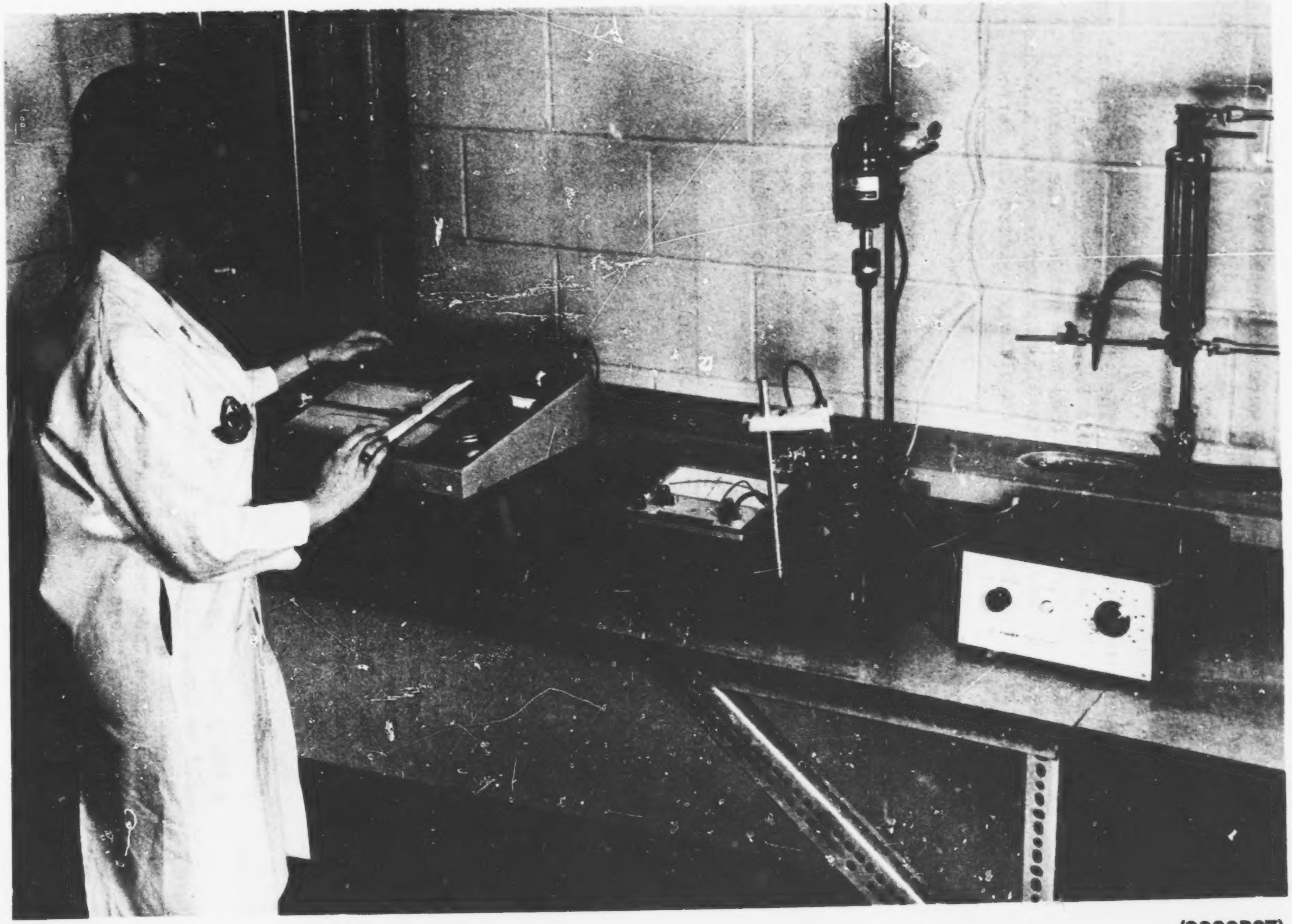
> Varying amounts of limestone and oxidizing agent (air or hydrogen peroxide) were added to 1500 ml of a synthetic coal mine water containing 220 ppm of Fe^{2+} added as ferrous sulfate and having the pH adjusted to 3.0 with sulfuric acid. The solution (mixture) was stirred continuously for a 5.5 hour period and changes in pH recorded with time. Samples were withdrawn periodically and analyzed for Fe^{2+}. The amount of limestone added was based on the acidity of the synthetic coal mine water; the amount of hydrogen peroxide was based on the concentration of Fe^{2+}. The apparatus for conducting these experiments is shown in Figure 2. An Orion Model 401 meter with a Sargent/Jena combination electrode was used to measure pH and a Houston Instrument Omnigraphic T-Y recorder, Model HR-80, was employed to record changes in pH.

Case I

Thirteen stones were tested. The amount of limestone added was twice the stoichiometric amount based on acidity of the synthetic coal mine water. This amount was selected from studies on batch-scale neutralization of actual coal mine water, (see Figure 13). The amount of limestone was also based on the assumption that the stones consisted of pure $CaCO_3$. The amount of hydrogen peroxide added was three drops, approximately 0.4 times the amount necessary to completely oxidize the ferrous iron present. The limestone was added at the start of the test. The H_2O_2 was added either (a) when pH reached 6.0 after addition of limestone (and would have continued to increase), or (b) when pH had leveled off at a value less than 6.0. In most instances, a coarse, a medium, and a fine fraction of each stone were tested.

Case II

Thirteen stones were tested. As in Case I, the amount of limestone added was twice the stoichiometric amount based on acidity of the synthetic coal mine water and was also based on the assumption that the stones consisted of pure $CaCO_3$. Three drops of 30 percent hydrogen peroxide were added, approximately 0.4 times the amount necessary to com-



(2030P27)

Figure 2. Apparatus for Neutralization of Synthetic and Actual Coal Mine Waters

pletely oxidize the ferrous iron present.

All experiments in Cases II-V were conducted with 325 x 400 mesh limestones, and with the limestone and the oxidizing agent (hydrogen peroxide or air) being added together.

Case III

Thirteen stones were tested. The limestone again was assumed to be pure $CaCO_3$, and the amount added was twice the stoichiometric amount based on acidity of the synthetic coal mine water. The amount of 30 percent peroxide added was increased to 0.5 ml, approximately 1.6 times the stoichiometric amount necessary to completely oxidize the ferrous iron present.

Case IV

Thirteen stones were tested. An excess amount, 0.5 ml, of 30 percent hydrogen peroxide was added, as in Case III. An adjustment was made in the amount of limestone to compensate for materials in the stones other than $CaCO_3$ or $MgCO_3$. The weight of limestone chosen was sufficient to provide twice the equivalent stoichiometric amount of pure $CaCO_3$ based on acidity. This amount was calculated using the formula:

$$Wt = \frac{(2X) \times 100}{(\%\ CaO) + (\%\ MgO)\ (56.08/40.32)}$$

where

Wt = weight of limestone in grams
X = stoichiometric amount of pure $CaCO_3$ based on acidity

Case V

Fourteen stones were tested. The amount of limestone added was twice the stoichiometric amount based on the acidity of the synthetic coal mine water and was also based on the assumption that the stones consisted of pure $CaCO_3$. Instead of adding hydrogen peroxide, air at a rate of 2500 ml/min was bubbled continuously into the solution through a fritted glass disk at the bottom of the beaker.

Batch-scale Neutralization of Actual Coal Mine Waters

A study was made of the conditions under which actual coal mine water could be neutralized with limestone on a batch scale. Using data from the preliminary study, a standardized procedure was chosen for batch-scale limestone neutralization of four actual coal mine waters--South Greensburg, Keystone, Tarrs, and Thorn Run. Differences in response of these waters to this standardized procedure were observed.

Compositional differences among the four waters were confirmed by elemental analysis.

Conditions for the neutralization experiments were: a sample of each water was treated on the same day as received in the laboratory, the first one at 18 C and then a second at 22 C. Temperature of the water as sampled ranged from 11 to 14 C. Twice the stoichiometric amount (based on determined acidity of the samples and assuming the limestone to be pure $CaCO_3$) of No. 1809 limestone, 325 x 400 mesh, was added to 1500 ml of the actual coal mine water in a 2000 ml beaker. Then for 90 minutes the mixture was stirred at a constant rate and aerated at 2500 ml/min with compressed air introduced through a medium porosity fritted glass disk. The apparatus used is illustrated in Figure 3.

A series of analyses was performed on 100 ml aliquots of each water (a) as received, (b) after treatment for 90 minutes, (c) after treatment for 90 minutes and having stood undisturbed overnight, and (d) after treatment for 90 minutes, having stood overnight, and then having been aerated and stirred for an additional 30 minutes.

Ferrous iron was determined colorimetrically using o-phenanthroline. Sulfates were determined gravimetrically. Acidity was determined by adding hydrogen peroxide, heating, and titrating to pH 8.2. Si, Al, Fe, Ca, Mg, Mn, and Na were determined using an emission spectograph. Eh was measured using platinum-calomel electrodes. Electromotive force (EMF) values were determined and converted to the standard hydrogen electrode scale (Eh) by the addition of the saturated calomel reference electrode potential, 242 millivolts. For the sake of conformity with most existing pertinent literature, the so-called European sign convention for electrode potentials was adopted; standard redox potentials for couples above hydrogen in the electromotive force series were given negative signs while those below were considered positive.

Conductivity was measured using a Hach conductivity meter, Model 2200. Dissolved oxygen was determined with a Yellow Springs, Model 54, oxygen meter equipped with a Clark-type membrane-covered polarographic probe. Turbidity was determined using a Hach laboratory turbidimeter. Dissolved solids were determined gravimetrically by evaporating a weighed amount of solution to dryness. The zeta potential was calculated from electrophoretic mobility data determined with a Zeta-Meter (Zeta-Meter, Inc., New York, New York). This instrument also allowed determination of conductivity with electrophoretic mobility.

Oxidation of Ferrous Iron

The objective of this study, to find a catalyst for the oxidation of ferrous iron in an acid medium, was carried out (a) by preparing a catalyst from coal, (b) by testing the prepared catalyst, (c) by testing commercially available activated carbons, and (d) by testing other materials which might have catalytic properties.

Catalyst Prepared from Coal

The first experiments dealt primarily with the development of satisfactory procedures for preparing an active material from coal. As a result of many experiments, the following procedure for making an active carbon evolved:

Devolatilization of minus 40 mesh coal at 500 to 800 C.
Crushing resultant coke to minus 40 mesh.
Activation in air of crushed coke at 300 to 600 C.
Calcination at 700 to 1000 C.

Test for Catalytic Activity

The standard test, developed to evaluate carbons and other materials as aids in the oxidation of ferrous iron, consisted of the following steps:

> A quantity (16 g) of the test material was washed twice with 20 ml portions of 6 N HCl, twice with 20 ml portions of deionized water, then washed two more times with a special test solution prepared by adding 200 ppm of ferrous iron as ferrous sulfate to deionized water and adjusting the pH to 3.0 with sulfuric acid. The washed material was then placed in a reactor tube (Figure 3), together with 150 ml of test solution. Air was bubbled at a selected rate into the mixture through a medium porosity fritted disk at the bottom of the reactor tube. The decrease in ferrous iron in the sample was determined periodically by dichromate titration using a Sargent Model D recording titrator. At the end of a specified period of time, the test solution was removed and 150 ml of fresh test solution added to start a new cycle or test.

Non-oxidative Neutralization and Addition of Coagulant Aids

Studies of the non-oxidative neutralization process involved: (a) precipitation of ferrous hydroxide from synthetic coal mine water by addition of lime, and measurement of electrophoretic mobility (zeta potential) of the precipitated ferrous hydroxide as formed and as changed by the addition of coagulant aids (electrolytes, polyelectrolytes, and inert solids); and (b) utilization of data from (a) in settling tests.

Materials

Synthetic Coal Mine Water

Fresh quantities of synthetic coal mine water were prepared as needed. Ferrous sulfate was added to deionized water to yield a solution containing 250 ppm of Fe^{2+}. The pH of the solution was then adjusted to 3.0 by addition of sulfuric acid.

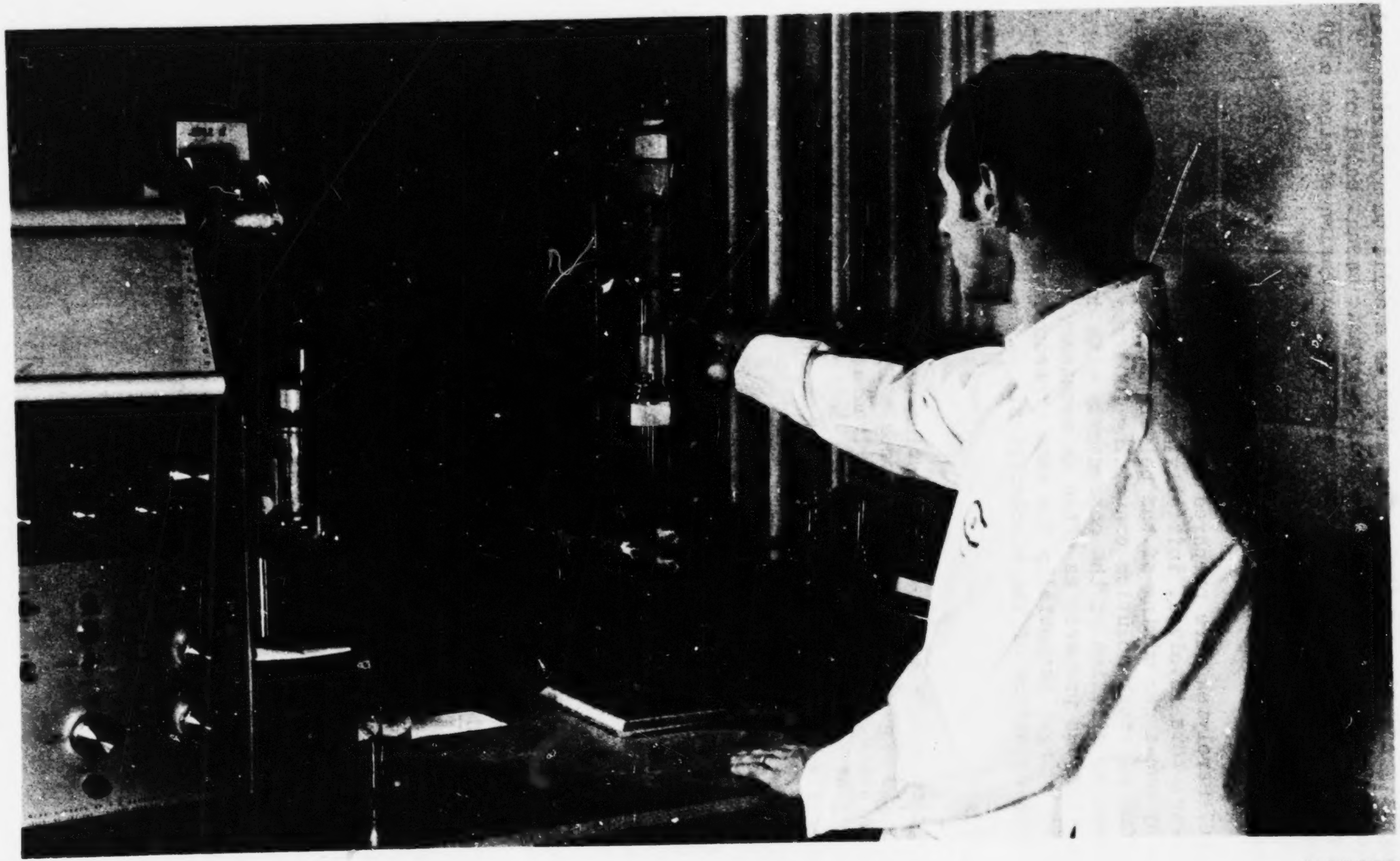


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Figure 3. Apparatus for Ferrous Iron Oxidation in the Presence of Coal-Derived Carbons

Ferrous Hydroxide Suspension

Reagent grade lime, $Ca(OH)_2$, was added as a solid to synthetic coal mine water in quantity equal to the stoichiometric amount based on acidity of the coal mine water. The resultant suspension attained a pH in the range 10.5 to 11.5.

Polyelectrolytes and Electrolytes

Polyelectrolytes were prepared according to specifications of the manufacturer; this involved, initially, preparation of a concentrated solution by non-shear mixing of the polyelectrolyte with deionized water. Then, a 1000 ml stock solution containing 1000 ppm of polyelectrolyte was prepared by dilution of the concentrate with deionized water. Fresh stock solution was prepared as often as necessary because of deterioration due to aging. Essentially the same procedure was employed in preparing stock solutions of the electrolytes.

Inert Solids

The inert solids selected for testing were: (a) M and D clay, a ball clay, (b) "red dog" collected from a pile of burned-out coal refuse material in Westmoreland County, Pennsylvania, and (c) fly ash collected from a stack at a pulverized coal-fired electric utility power station. These materials were added as solids without further preparation.

Electrophoretic Mobility Studies

Selected amounts of coagulant aids were added to 100 ml portions of ferrous hydroxide suspension and stirred for one minute. Electrophoretic mobility of the resultant mixture was then measured and a graph prepared of the observed zeta potential values versus concentration of each coagulant aid.

In certain tests, the inert solid was added to synthetic coal mine water first, followed by lime, and then finally by the polyelectrolyte.

Settling Rate Studies

Coagulant aids were added to 2000 ml of ferrous hydroxide suspension; the entire mixture was stirred for one minute, and then transferred to a 2000 ml graduated cylinder. The line of demarcation between solids and water was observed periodically for times up to 2.5 hours.

Magnetic Sludge Studies

To explore conditions under which a magnetic sludge can be formed during coal mine water neutralization, tests were conducted using both synthetic and actual coal mine water. The following procedure for these tests was adopted:

Synthetic test solutions were prepared by adding specified amounts of ferrous sulfate to deionized water and adjusting the pH to 3.0 with sulfuric acid. Test samples of actual mine water were obtained from either the South Greensburg or the Keystone discharge.

A 1500 ml sample of test solution was transferred to a 2000 ml beaker; then a mechanical stirrer, thermometer, and EMF and pH electrodes were introduced. Slow, constant-speed stirring was commenced, and initial values of Eh, pH, and temperature were recorded. Either 1N NaOH solution or solid hydrated lime, $Ca(OH)_2$, was added to precipitate ferrous hydroxide. Eh, pH, and temperature were recorded at the start and periodically thereafter at about 15 minute intervals. Stirring was stopped momentarily while changes in Eh, pH, temperature, magnetic response (determined qualitatively with a small permanent magnet), and color of the precipitate were observed. In cases where aeration was utilized to accelerate the oxidation of ferrous iron, air flow was measured with a small rotameter. The rate of stirring was held constant in all runs.

The effects of reaction pH, impurities, reaction temperature, and sludge concentration on formation of magnetic sludge were noted.

Miscellaneous Studies

Effect of Coagulant Aids on $Fe(OH)_3$

The effect of selected coagulant aids on zeta potential of ferric hydroxide resulting from limestone neutralization of synthetic coal mine water was examined.

The ferric hydroxide was prepared in the following manner: Limestone No. 1809, 325 x 400 mesh, was added to 1500 ml of synthetic coal mine water containing 250 ppm of Fe^{2+} and adjusted to pH 3.0 with sulfuric acid. The amount of limestone used was twice the stoichiometric amount based on acidity of the synthetic coal mine water sample. Conversion of the ferrous iron to ferric hydroxide, $Fe(OH)_3$, was completed in 90 minutes by aeration. Final pH of the mixture was 7.8.

Various amounts of selected coagulant aids were added to 100 ml aliquots of the resultant ferric hydroxide-limestone mixtures. Electrophoretic mobility of the sludge particles was then measured using a Zeta-Meter; a graph was prepared of calculated zeta potential values versus concentration of each coagulant aid.

Flotation Studies

A limited study involving separation of ferric hydroxide formed by limestone neutralization of actual coal mine water was conducted utilizing standard froth flotation equipment and procedures. Samples (2500 ml) of limestone-neutralized South Greensburg discharge obtained from continuous flow apparatus experiments were stirred and aerated at constant rates in a sub-aeration type Wemco Fagergren apparatus. Selected froth promoters, sample conditioners, and coagulant aids were added in various combinations. The amount of sludge solids that reported to the froth and tailings was then determined.

Calcium Ion Electrode Studies

The calcium ion electrode was investigated for use in measuring the solubility of limestones in mine water. A calibration curve was prepared using solutions of pure $CaCl_2$ with concentrations from 1×10^{-1} to 1×10^{-3} M. Activity or concentration of Ca^{2+} ion versus the electrode potential as measured with the Orion calcium ion electrode was plotted on semi-log graph paper.

ASTM Activities

As members of ASTM Committee D-19 on Water, project personnel participated in the development and round robin testing of a method for determination of acidity "specifically for mine drainage, surface streams receiving mine drainage, industrial waste acids and their salts, and similar waters bearing substantial amounts of ferrous iron or other polyvalent cations in a reduced state."

The round robin sampling, testing, and compilation of data have not been completed by the committee. If satisfactory results are obtained in the round robin, the method is to be proposed as a tentative standard at the January 1970 ASTM D-19 meeting.

Continuous Flow Tests

A continuous flow test apparatus was designed and constructed for use in evaluating the limestone neutralization process.

Figure 4 is an artist's conception of the continuous flow system. A photograph of the actual system is shown in Figure 5. A description of materials, equipment, and operation follows:

Reservoir: The reservoir has a total capacity of 210 gallons and consists of two Glascote glass-lined tanks each having bottom discharge and lids. The tanks have 150-gallon and 60-gallon capacities.

Sample Cooling and Circulating System: A Forma "Forma-Temp" portable cooler is used to maintain the sample at temperatures as low as 46 F. The cooler has a rated capacity of 4000 Btu/hr. Circulation of the sample between the two reservoirs is accomplished by use of a Gorman Rupp Model 11698, 5600 Series pump, with a Gorman Rupp Model 12500-21 oscillating pump used for priming.

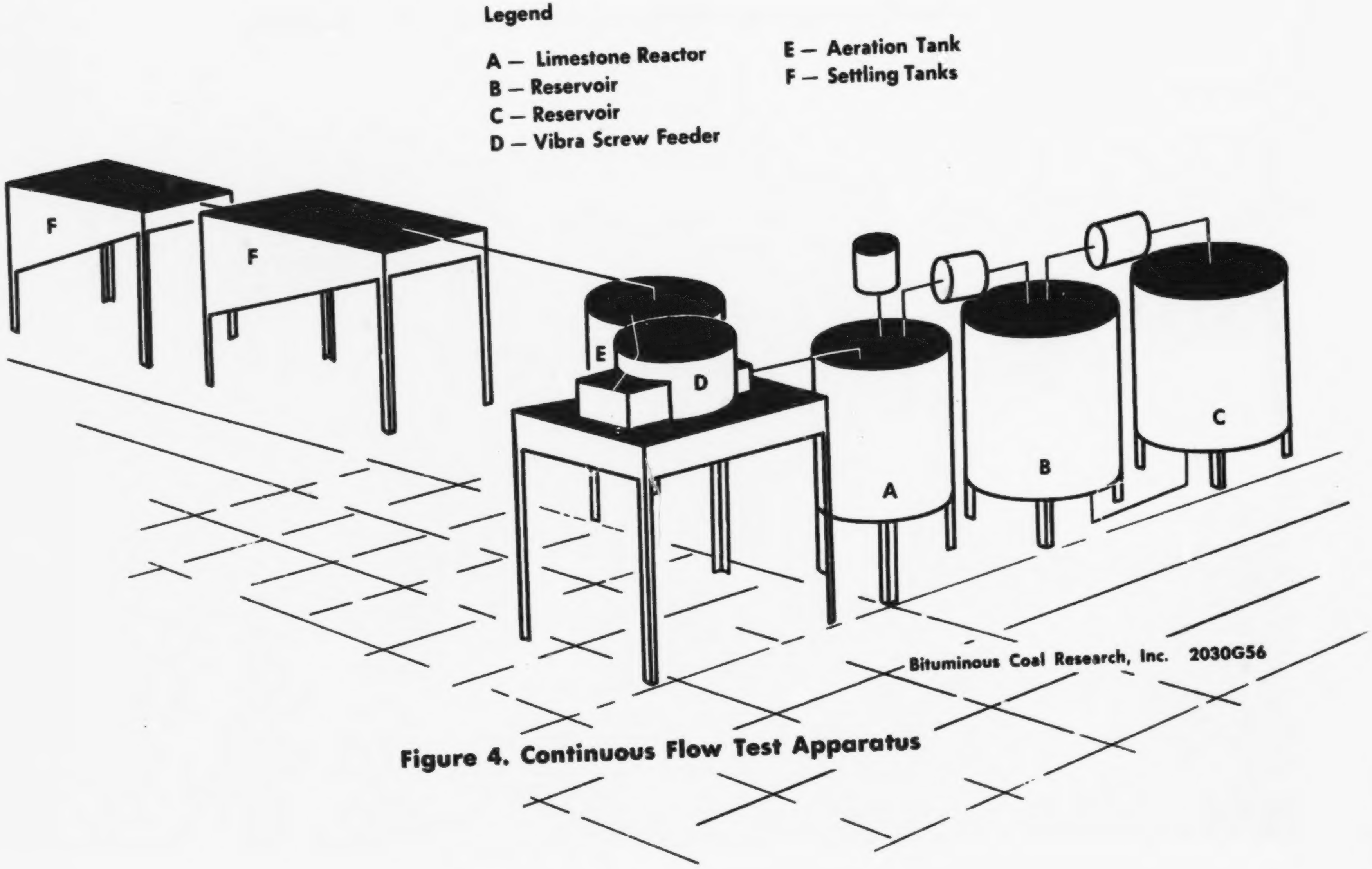
Legend
A — Limestone Reactor
B — Reservoir
C — Reservoir
D — Vibra Screw Feeder
E — Aeration Tank
F — Settling Tanks
F
F
E
D
A
B
C

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Figure 4. Continuous Flow Test Apparatus

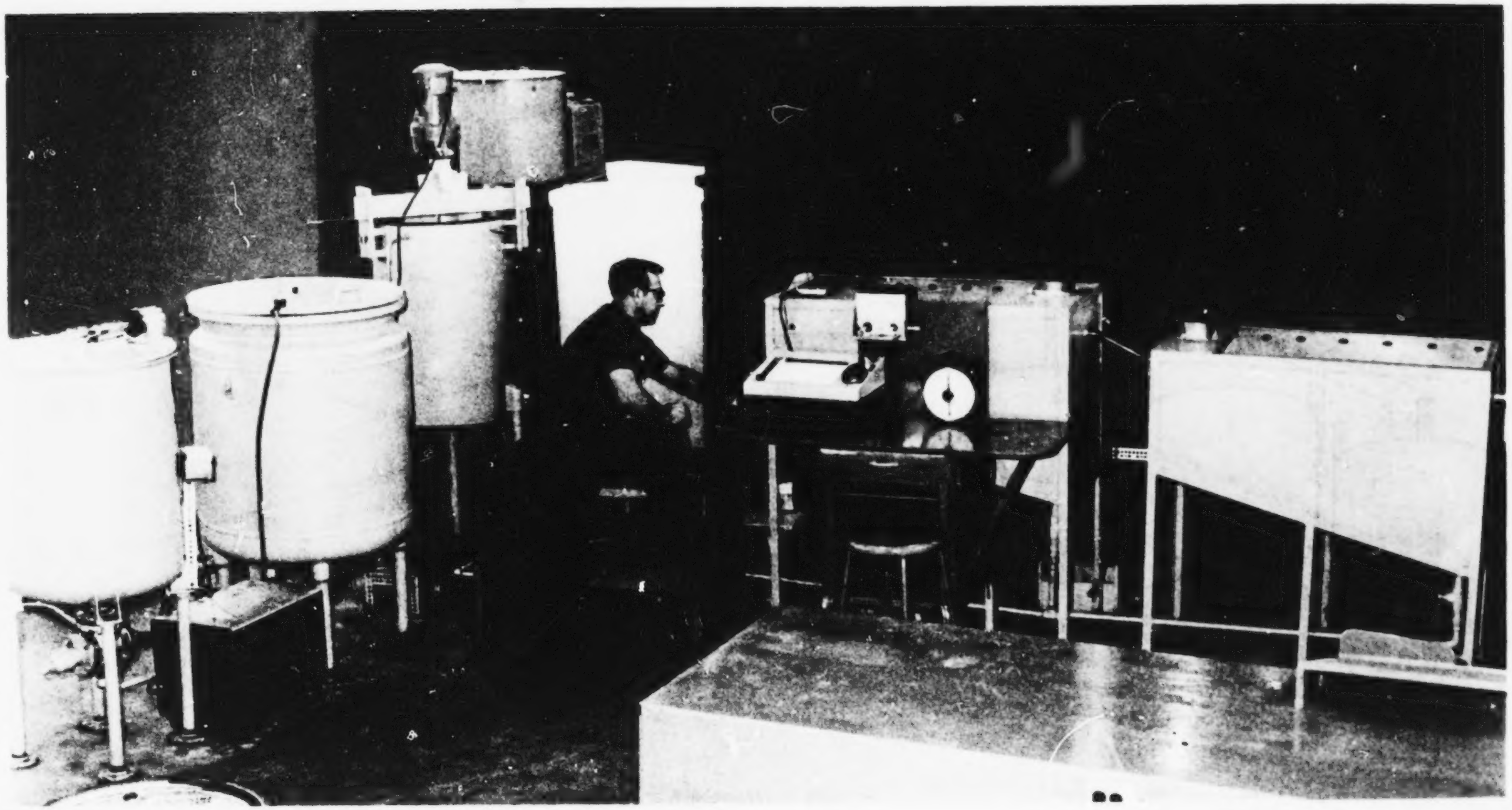

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Figure 5. General View of Continuous Flow System

Limestone Reactor: The stirred tank reactor consists of a 60-gallon stainless steel tank equipped with four 2-inch stainless steel baffles. Stirring is accomplished by use of a "Lightnin" Model ND-1A 1/4 horsepower, 1750 rpm motor, 350 rpm propeller, portable mixer equipped with two 7.7-inch diameter propellers. The sample is transferred to the stirred tank reactor from the reservoir using a Gorman Rupp Model 11698, 5600 Series pump. The flow rate is controlled by a 1/2-inch Whitey Model 1RS8-316 stainless steel needle valve, and is measured by a Brooks Model 1305 flowmeter. Compressed air is introduced into this tank through a manifold consisting of 4 spherical gas diffuser stones (Fisher Scientific) mounted at the end of 3/16-inch stainless steel tubing.

Limestone Feeder: Pulverized limestone is fed to the reactor by a Vibra Screw feeder equipped with a 1/4-inch diameter feed screw.

Aeration Tank: The polyethylene cylindrical tank has a capacity of 80 gallons and has an air manifold identical to the one mentioned above. Gravity flow from the stirred tank reactor into the aeration tank is controlled by a polypropylene ball valve.

Activated Carbon Reactor: The circular, 14-inch diameter stainless steel basket is 4 inches deep and is divided into four quarters. Carbon is equally distributed into four sections and held loosely with porous cloth. The entire apparatus is covered with 18 mesh stainless steel woven wire cloth and is immersed in the aeration tank a few inches above the gas diffuser stones.

Settling Tanks: Two 90-gallon settling tanks are used to collect the sludge. These tanks are constructed of 316 stainless steel.

Piping: Piping is stainless steel, except for the large diameter flexible Tygon connectors between the settling tanks.

An auxiliary portable pumping system consists of a Gorman Rupp Model 11698, 5600 Series, and a Gorman Rupp Model 12500-21 oscillating pump.

The general procedure used for treating coal mine water in this system follows:

A total of 125 gallons of coal mine water was treated over a 2.5 hour period under flow conditions. The limestone reactor was filled initially with 50 gallons of coal mine water, the appropriate amount of limestone added, and the mixture stirred for 50 minutes.

After this initial period, the flow of coal mine water was adjusted to 1 gpm both from the reservoirs to the limestone reactor and from the limestone reactor to the aeration tank.

Additional limestone was added at a constant rate of twice the stoichiometric amount based on acidity.

Compressed air was fed into the aeration tank as it was being filled to the 50 gallon mark; aeration was continued and the level held at 50 gallons by pumping the aerated sample into the settling tank. Water remaining in the aeration tank at the end of the test was pumped into the settling tanks.

Aliquots (200 ml) were withdrawn periodically from the mixing tank, the aeration tank, and the two settling tanks; the pH and ferrous iron concentration were determined on each.

DISCUSSION

Assessment of Coal Mine Water Composition

Analytical data covering the four coal mine waters selected for study on this program are given in Table 1. Although every coal mine discharge is unique, these four discharges represent three significant categories for purposes of this study: South Greensburg and Keystone discharges represent category (a), a ferrous iron water containing little or no aluminum; Tarrs falls into category (b), a ferrous iron water containing a substantial amount of aluminum. The Thorn Run discharge represents category (c), a ferric iron water.

Evaluation of Limestones

Limestone is a general term embracing carbonate rocks or fossils; it is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and aluminum (11). If "limestone" is to be used as a neutralizing agent for coal mine water, the questions arise as to which type of limestone, or are all limestones equally effective?

To attempt to answer these questions, various types of limestones were secured specifically for this study. They are listed in the order received, in Table 2, together with the reasons for their selection.

A series of neutralization reactions was devised to measure the pH response (reactivity) resulting from addition of these stones to a synthetic coal mine water (acidified ferrous sulfate solution); a suitable oxidizing agent was also added. Differences in pH response were then related to the chemical composition and physical properties of the limestone.

Chemical Properties of the Limestones

Table 3 contains a summary of the analyses of the thirteen limestones originally selected for study. These analyses were performed on the overall batch of limestone as received and were used in evaluating the experiments listed below under Case I through Case IV.

After completion of Case IV experiments, the analyses were repeated on the narrow particle size range material used in Case II through V experiments. The results of these analyses are listed in Table 4. Limestone No. 1462 was added to the list as an example of a magnesite, $MgCO_3$, because experimental evidence obtained during the

TABLE 1. ANALYSES OF THREE GENERAL CATEGORIES OF COAL MINE WATER SELECTED FOR STUDY

Category	Source	pH	Spectrographic Analysis, ppm							Fe^{2+} % of Total Fe	Acidity, ppm as $CaCO_3$	SO_4^{2-}, ppm
			Fe	Al	Mn	Ca	Mg	Si	Na			
a	South Greensburg	4.7	123	8	4	210	74	14	88	91	250	1140
a	Keystone	6.0	330	<3	4	235	94	7	1000	95	265	3630
b	Tarrs	2.7	122	55	4	194	83	41	--	79	752	1474
c	Thorn Run	2.4	168	102	16	192	78	28	38	5	1285	1944

TABLE 2. LIMESTONES SELECTED FOR STUDY

BCR Sample No.	Source	Reason for Choice
1335	Hills Material Co. Rapid City, South Dakota	Good performance in air pollution studies at BCR
1337	Mineral Pigments & Metals Chas. Pfizer Gibsonburg, Ohio	High Mg
1352	H. E. Millard Lime & Stone Co., Inc. Annville, Pennsylvania	High Mg
1355	Elkins Limestone Elkins, West Virginia	High Si
1362	Nickajack Dam-Fernvale Co. Limestone TVA	High Fe
1364	Giant Portland Cement Co. Egypt, Lehigh County, Pa.	High Al
1461	Basic, Inc. Gabbs, Nevada	First thought to be a magnesite, later proved to be a dolomite
1462	Basic, Inc. Gabbs, Nevada	Magnesite
1654	J. E. Baker Co. York, Pennsylvania	Poor performance in air pollution studies at BCR
1809	Winfield Lime & Stone Co., Inc. West Winfield, Pennsylvania	Used at Rochester & Pittsburgh Coal Co. for coal mine water neutralization
2135	Appalachian Stone Co. Lake Lynn Plant Mercersburg, Pennsylvania	Used by Bureau of Mines for coal mine water neutralization studies
2136	Greer Limestone Co. Greer, West Virginia	Used by Bureau of Mines for coal mine water neutralization studies
2145	McClout Yards Marine City, Michigan	Used in SO_2 removal tests at an electric power generation plant
2177	German Valley Limestone Co., Riverton, West Virginia via Mr. Ronald Hill	Used at Norton Mine Drainage Treatment Laboratory

TABLE 3. ANALYSES OF THIRTEEN LIMESTONES ORIGINALLY SELECTED FOR STUDY. CASE I THROUGH CASE IV

BCR Sample No.	Spectrochemical Analyses, Mineral Samples Reported as Percent by Weight of Ignited Sample (900 C)									
	Loss on Ignition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
1335	42.9	3.2	0.67	0.38	0.69	94.0	0.05	0.02	<0.1	<0.03
1337	47.5	0.78	0.15	0.25	45.0	53.0	0.02	<0.02	<0.1	<0.03
1352	43.2	7.4	2.31	1.85	30.0	56.0	0.14	0.08	0.77	<0.03
1355	33.3	27.5	5.75	2.48	1.85	60.0	0.33	0.44	0.87	0.05
1362	33.6	15.2	3.70	21.0	3.20	55.0	0.29	0.08	0.66	0.44
1364	33.1	23.1	8.20	2.60	3.30	58.0	0.35	0.61	1.40	0.08
1461	50.2	2.61	0.45	0.86	90.0	4.35	0.03	0.02	0.10	0.03
1654	46.0	2.56	0.61	1.87	36.0	58.0	<0.05	0.08	<0.1	0.14
1809	41.5	5.90	1.99	1.50	1.34	88.0	0.07	0.07	0.28	0.14
2135	35.6	19.4	5.40	2.38	2.55	68.0	0.23	0.36	1.03	0.03
2136	37.3	15.4	4.10	1.78	2.90	71.0	0.18	0.46	0.79	0.03
2145	41.4	2.05	0.60	0.48	1.69	92.0	0.04	0.03	<0.1	0.03
2177	43.0	1.0	0.43	0.15	1.16	97.0	0.04	0.02	<0.1	<0.03

TABLE 4. ANALYSES OF FOURTEEN LIMESTONES SELECTED FOR STUDY.
CASE V

Spectrochemical Analyses, Mineral Samples
Reported as Percent by Weight of Ignited Sample (900 C)

BCR Sample No.	Loss on Ignition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	MnO_2
1335	42.8	3.35	0.77	0.33	0.72	94.0	0.05	0.02	<0.1	<0.03
1337	46.5	1.40	<0.3	0.32	43.0	55.0	<0.03	<0.02	<0.1	<0.03
1352	42.6	8.00	2.75	1.08	30.0	56.0	0.11	0.08	0.87	<0.03
1355	34.0	25.5	4.40	1.95	1.80	64.0	0.25	0.40	0.91	0.03
1362	36.1	10.6	2.17	12.8	3.80	69.0	0.12	0.03	0.20	0.37
1364	30.4	28.5	10.7	3.70	4.20	46.5	0.50	0.70	2.25	0.07
1461	47.2	1.05	<0.3	0.30	45.0	53.0	<0.03	<0.02	<0.1	<0.03
1462	48.4	3.90	1.24	1.46	80.0	11.5	0.03	<0.02	<0.1	<0.03
1654	45.8	2.05	0.54	1.83	38.0	56.0	<0.03	<0.02	<0.1	<0.03
1809	42.1	4.60	1.50	1.30	1.06	89.0	0.05	0.02	0.12	0.12
2135	34.6	19.5	6.10	2.70	2.40	66.0	0.27	0.33	1.50	0.03
2136	36.7	15.8	4.40	1.70	2.80	72.0	0.23	0.36	0.62	0.03
2145	41.7	5.00	1.69	0.88	1.48	90.0	0.07	0.03	<0.1	<0.03
2177	42.7	1.41	0.42	<0.3	0.90	95.0	<0.03	0.02	<0.1	<0.03

Case I through Case IV experiments indicated that sample No. 1461 was not a magnesite.

Table 5 contains the results of x-ray analyses on the fourteen limestones selected for study. This analysis indicates only the structure of compounds present. The amount of each compound present cannot be obtained from these data. Those compounds present in relatively small amounts may not be detected at all.

Physical Properties of the Limestones

Density and surface area of the limestones tested in these experiments are listed in Table 6. In cases where surface area was measured by both the standard and the modified BET technique, agreement between the two methods was good. Limestone No. 2135 has greater than 11 times the surface area of limestone No. 1337, even though the particle size of each limestone was 37 to 44 microns (325 x 400 mesh).

Neutralization Reactions

The results of the five series of neutralization tests, Case I through Case V, are as follows:

Case I

The type of neutralization curve produced by the addition of finely divided (minus 325 mesh) limestone, BCR No. 1809, to synthetic coal mine water is shown in Figure 6. A pH of 6.0 was attained within 3 minutes after limestone addition. At that time H_2O_2 was added, and the pH decreased initially as a result of the oxidation of ferrous iron to the ferric, Fe^{3+}, state. After oxidation was complete, the neutralizing ability of the limestone then became the controlling factor and the pH again increased to a maximum of 7.7.

Figure 7 illustrates a less effective limestone, BCR No. 1337. After addition of this limestone to synthetic coal mine water, the pH leveled off at a maximum of 5.6. Addition of H_2O_2 resulted in a decrease in pH due to ferrous iron oxidation, but recovery of pH was not rapid. Maximum pH recorded after addition of peroxide was only 5.5.

Each of the other stones was tested in similar fashion. All data from this Case I series of tests and the respective particle size fractions of limestones used are listed in Table 7.

The effect of particle size is most noticeable. The coarser sizes--50 x 60, or 60 x 100 mesh--show much slower and incomplete neutralization than the more finely divided sizes--325 x 400 mesh or minus 400 mesh--of the same limestone. Maximum pH attained after oxidation as well as time of maximum pH attainment after limestone

TABLE 5. X-RAY ANALYSES OF FOURTEEN LIMESTONES

BCR Sample No.	Compounds Identified
1462	$MgCO_3$, $CaMg(CO_3)_2$
1337	$CaMg(CO_3)_2$
1461	$CaMg(CO_3)_2$
1654	$CaMg(CO_3)_2$, $CaCO_3$
1352	$CaMg(CO_3)_2$, $CaCO_3$
1364	$CaCO_3$, SiO_2, $[6SiO_2 \cdot Al_2O_3 \cdot 9MgO \cdot 7H_2O]$
1355	$CaCO_3$, SiO_2
1362	$CaCO_3$, SiO_2, $\alpha\text{-}Fe_2O_3$, $Ca(MgFe)(CO_3)_2$
2136	$CaCO_3$, SiO_2
2135	$CaCO_3$, SiO_2
1335	$CaCO_3$
2145	$CaCO_3$, SiO_2
1809	$CaCO_3$, SiO_2
2177	$CaCO_3$

TABLE 6. DENSITY AND SURFACE AREA OF FOURTEEN LIMESTONES

BCR Sample No.	Density, D, g/ml	Surface Area, SA, m^2/g
1335	2.70	0.88*
1337	2.74	0.62*
1352	3.57	2.29‡
1355	2.63	2.94‡
1362	3.02	2.53‡
1364	2.87	2.13*
1461	2.94	1.11‡
1462	3.27	1.98‡
1654	2.32	1.22*
1809	3.18	1.76*, 1.72‡
2135	2.64	7.18‡
2136	2.46	5.39*, 5.13‡
2145	2.59	2.05‡
2177	2.54	1.17‡

* Standard BET

‡ Modified BET

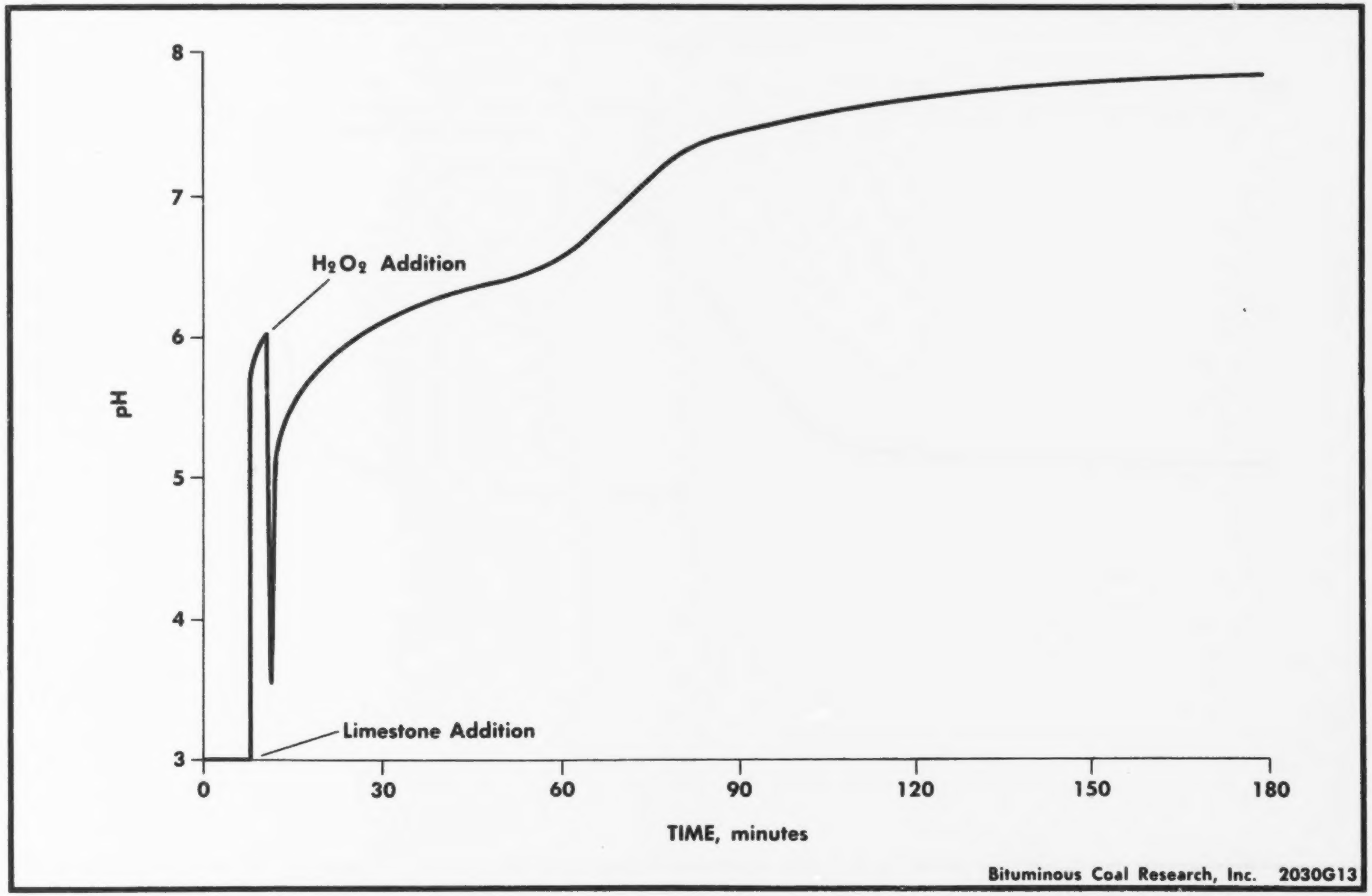

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Figure 6. Neutralization of Synthetic Coal Mine Water with No. 1809 Limestone

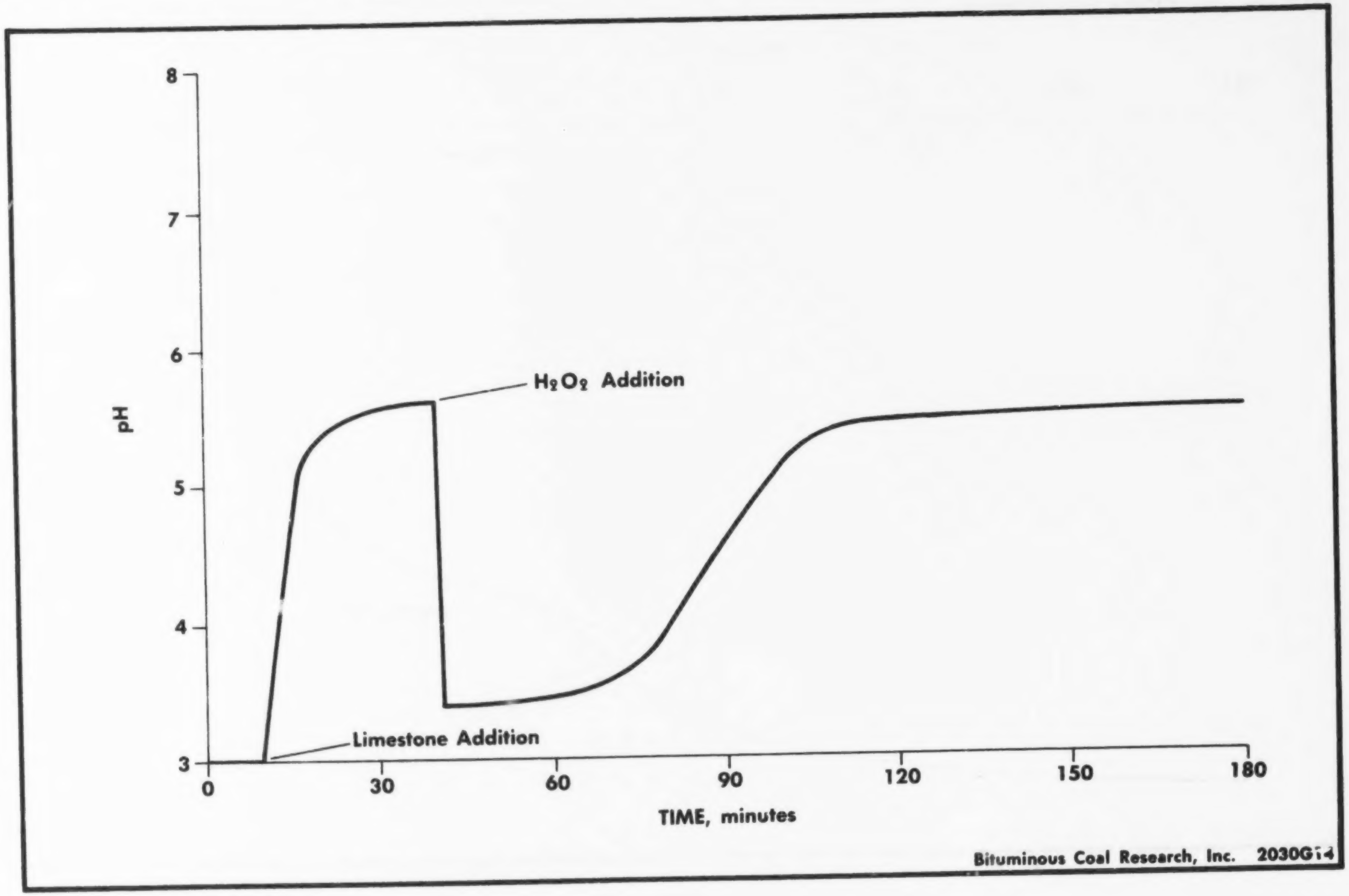

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Figure 7. Neutralization of Synthetic Coal Mine Water with No. 1337 Limestone

TABLE 7. EFFECT OF PARTICLE SIZE OF LIMESTONES ON pH OF SYNTHETIC COAL MINE WATER. CASE I*

			After Limestone Addition				
			Before H_2O_2 Addition		After H_2O_2 Addition		
BCR Sample No.	Mesh Size Tested	Original pH of Synthetic Mine Water	Maximum pH Attained	Time after Limestone Addition, min	Minimum pH Attained	Maximum pH Attained after Oxidation	Time of Maximum pH after H_2O_2 Addition, Min
1335	-400	2.8	6.0	5	3.9	7.9	160
	140 x 200	3.0	5.9	15	3.4	5.6	42
	50 x 60	3.0	5.8	28	3.2	5.3	64
1337	-400	3.0	5.6	25	3.2	5.5	96
	140 x 200	3.1	5.8	70	3.4	5.5	140
	50 x 60	3.0	5.5	120	3.1	5.0	240
1352	-400	3.1	6.1	6	3.6	5.8	85
	100 x 140	2.9	5.9	26	3.2	5.3	128
	50 x 60	3.1	5.8	44	3.1	3.2	40
1355	-400	3.0	6.1	5	4.5	7.7	122
	140 x 200	3.0	6.0	22	3.7	5.7	24
	50 x 60	3.0	5.9	32	3.6	5.4	38
1362	-400	3.0	6.2	12	3.7	7.5	240
	140 x 200	3.1	6.2	12	3.4	5.6	86
	50 x 60	2.9	6.0	30	3.2	5.7	105
1364	-400	3.0	6.2	6	3.8	7.6	222
	140 x 200	3.0	6.1	16	3.4	5.5	44
	50 x 60	3.0	6.0	36	3.4	5.2	105
1461	325 x 400	3.0	5.6	9	3.1	5.3	50
	100 x 140	3.0	5.6	45	3.2	5.0	120
	50 x 60	3.0	5.4	70	2.9	3.1	93
1654	325 x 400	2.9	5.9	14	3.2	5.3	50
	200 x 325	2.9	5.7	22	3.3	5.3	45
	60 x 100	3.0	5.6	44	3.1	3.2	40
1809	-325	2.9	6.0	3	3.9	7.7	100
	100 x 200	3.0	5.9	3	3.9	7.9	110
	60 x 100	3.0	5.9	12	3.5	5.6	54
2135	-400	3.0	6.0	1	4.2	7.6	187
	140 x 200	3.0	6.0	5	4.0	6.5	20
	50 x 60	3.0	6.0	17	3.7	5.5	20
2136	-400	3.0	6.0	2	4.2	7.8	211
	140 x 200	3.0	6.0	3	3.9	7.5	186
	50 x 60	3.0	5.9	25	3.4	5.3	55
2145	325 x 400	3.0	6.0	3	3.9	7.8	100
	60 x 100	3.0	6.2	4	4.1	7.7	88
2177	325 x 400	3.0	6.1	2	3.8	7.8	118

* Insufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added after the limestone.

addition, but prior to oxidation, are the best indicators of effective neutralization for this series of experiments.

Using these criteria, the stones have been grouped in three general categories: Group A, the most effective neutralizing agents--No. 1335, 1355, 1809, 2135, 2136, 2145, and 2177; Group B, intermediate--No. 1362 and 1364; and Group C, the least effective neutralizing agents--No. 1337, 1352, 1461, and 1654.

An interesting trend is shown in Table 8. The pH attained one hour after addition of H_2O_2, before equilibrium (complete ferrous iron oxidation) had been attained, was arbitrarily chosen as an indication of neutralizing efficiency. With few exceptions, neutralizing efficiency of a stone decreases as the percentage of MgO present in the stone increases.

No similar trend is apparent with percentage of CaO present; for example, stones No. 1654 and 1355 have similar CaO contents yet are widely spaced in Table 8. More is involved than mere high calcium oxide content. No other trends could be found from chemical composition and neutralization efficiency. The data, however, show limestones to be more effective than dolomites or magnesites.

Case II

Figures 8, 9, and 10 represent the pH curves generated by 325 x 400 mesh samples of all the test limestones when the oxidant was added at the same time as the limestone to synthetic coal mine water. The stones have been grouped according to overall appearance of the curve rather than the pH attained at one point in time or some other arbitrary standard. Figure 11 (one of the curves from Figure 8) shows that ferrous iron has not been completely oxidized by the addition of 3 drops of hydrogen peroxide, the amount used in this test. Figure 11 also reveals the reason for the inflections in these curves. The initial effect of the addition of limestone was an increase in pH. Then the oxidation of ferrous iron retarded the pH increase until all the iron was oxidized; the system was then allowed to achieve maximum pH as a result of the neutralizing action of the limestone present. Those limestones represented in Figures 9 and 10 produced a pH greater than 7 only after several days subsequent to ferrous iron oxidation.

The test data are listed in Table 9; the 13 limestones tested are arranged in order of increasing reactivity to coal mine water or efficiency based on Figures 8, 9, and 10. A mathematical relationship was noted between efficiency and some property or combination of properties of the limestones. Efficiency, in this case, is directly related to area under the individual curves in Figures 8, 9, and 10; the greater the area, the greater change in pH as a result of limestone addition. Reactivity in this context is synonymous with efficiency.

TABLE 8. EFFECT OF MAGNESIUM CONTENT OF LIMESTONE ON pH, ONE HOUR AFTER NEUTRALIZATION AND OXIDATION. CASE I*

BCR Sample No.	pH Attained One Hour after H_2O_2 Addition	Spectrochemical Analyses, MgO Percent of Ignited (900 C) Sample
1461	5.3	90.0
1337	5.3	45.0
1654	5.3	36.0
1352	5.8	30.0
1364	6.0	3.30
1362	6.0	3.20
2135	6.1	2.55
2136	6.3	2.90
1335	6.4	0.69
1355	6.6	1.85
2177	6.6	1.16
2145	7.0	1.69
1809	7.3	1.34

* Insufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added after the limestone.

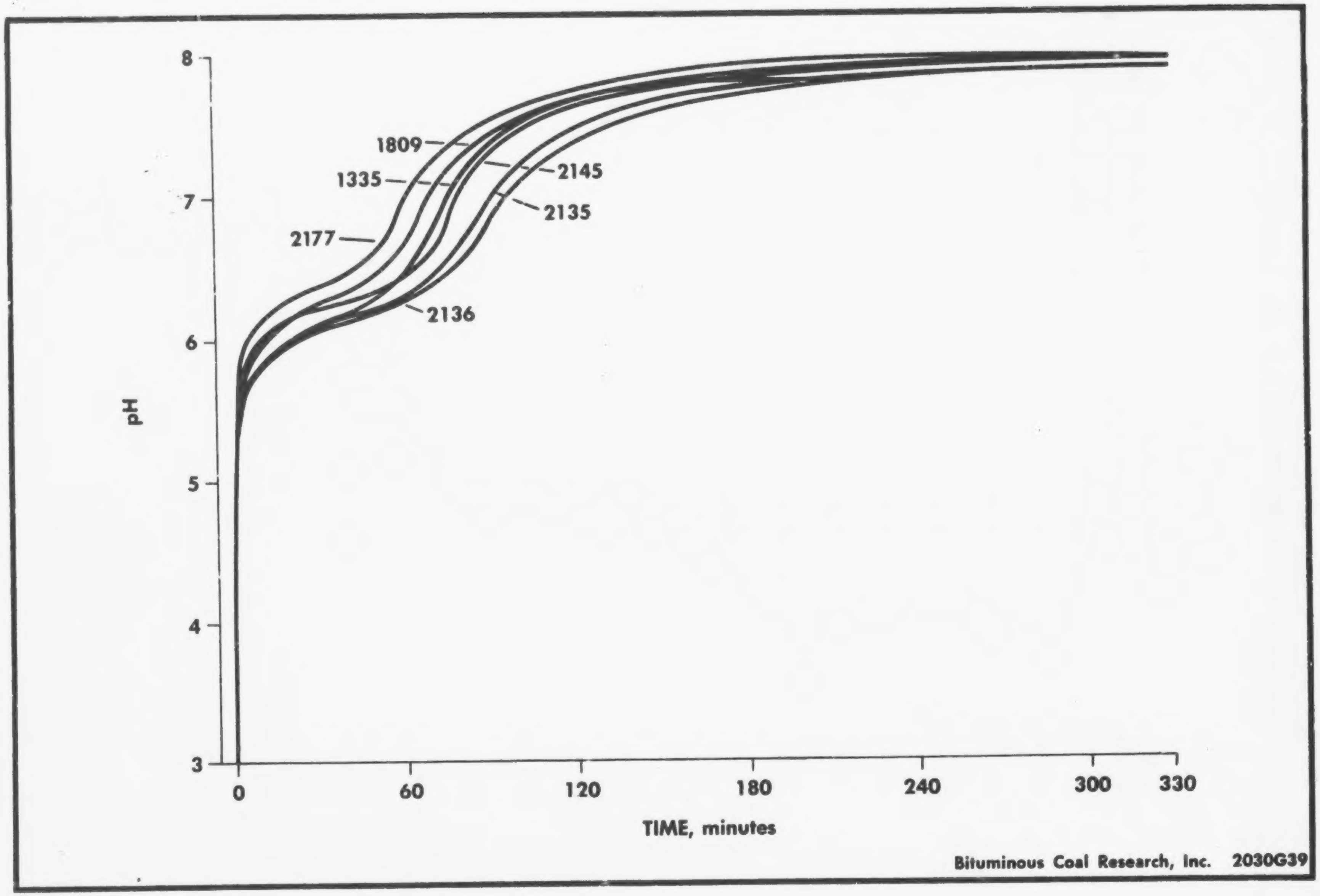

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Figure 8. Effect of Group A Limestones on Synthetic Coal Mine Water

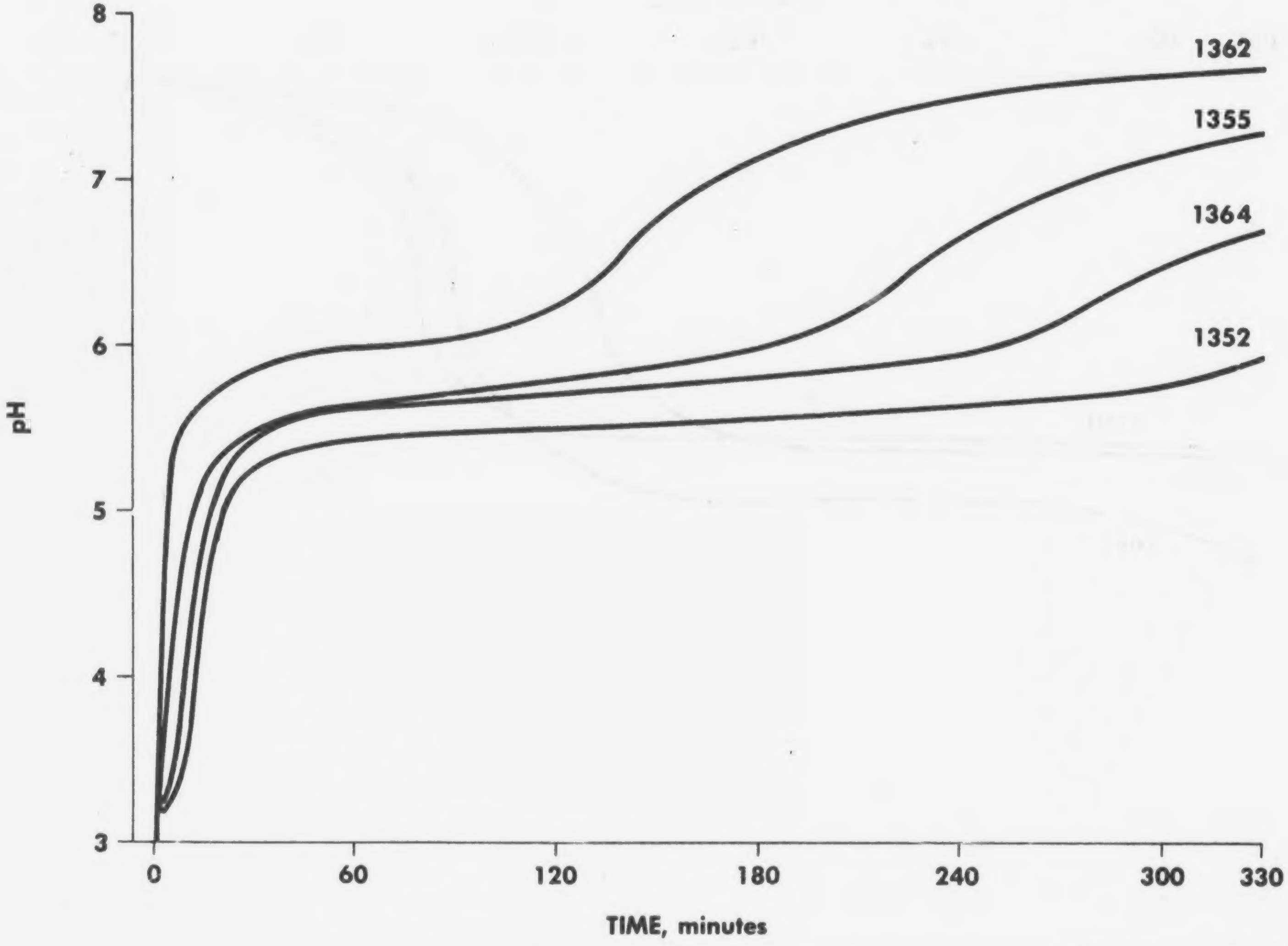

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Figure 9. Effect of Group B Limestones on Synthetic Coal Mine Water

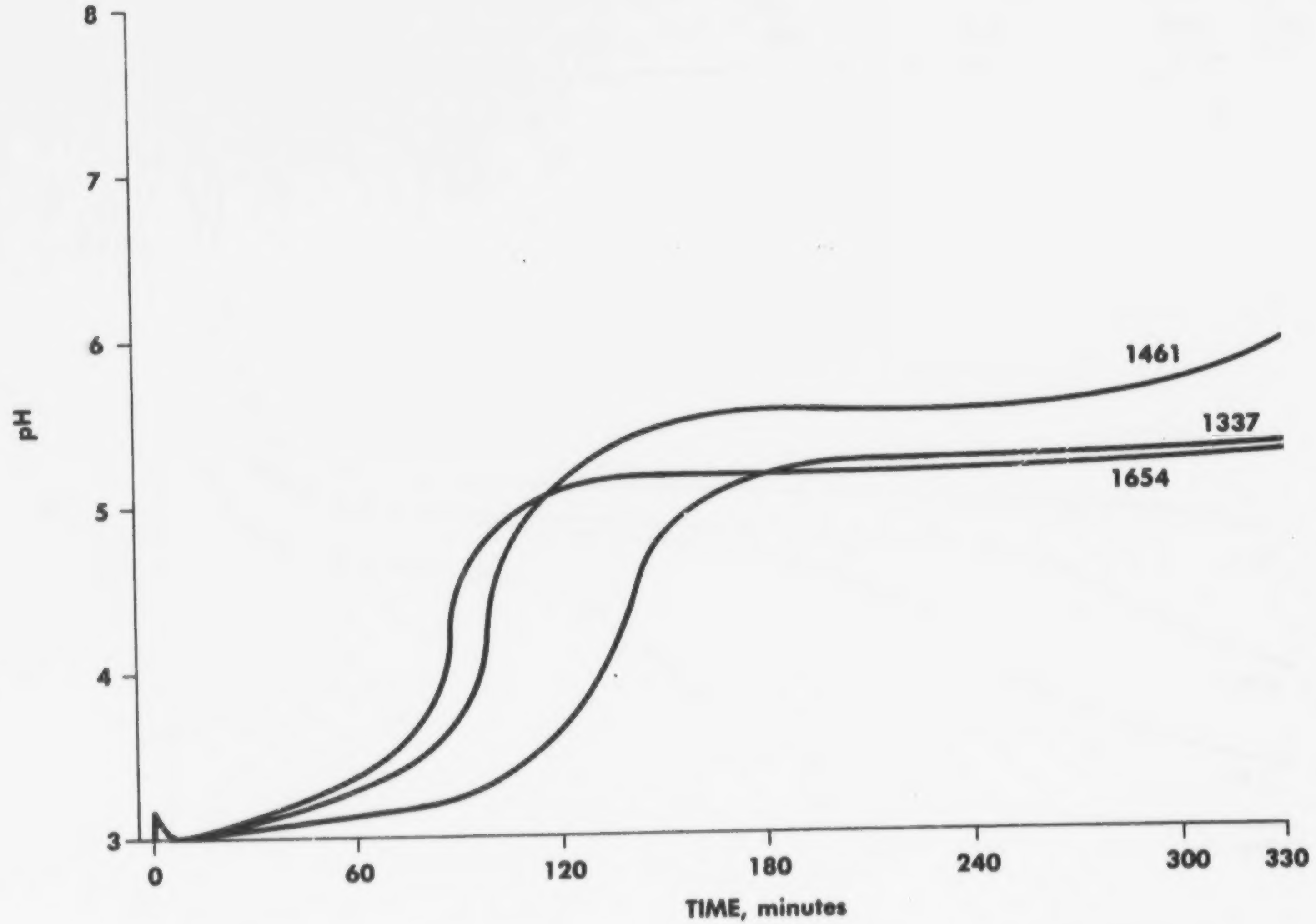

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Figure 10. Effect of Group C Limestones on Synthetic Coal Mine Water

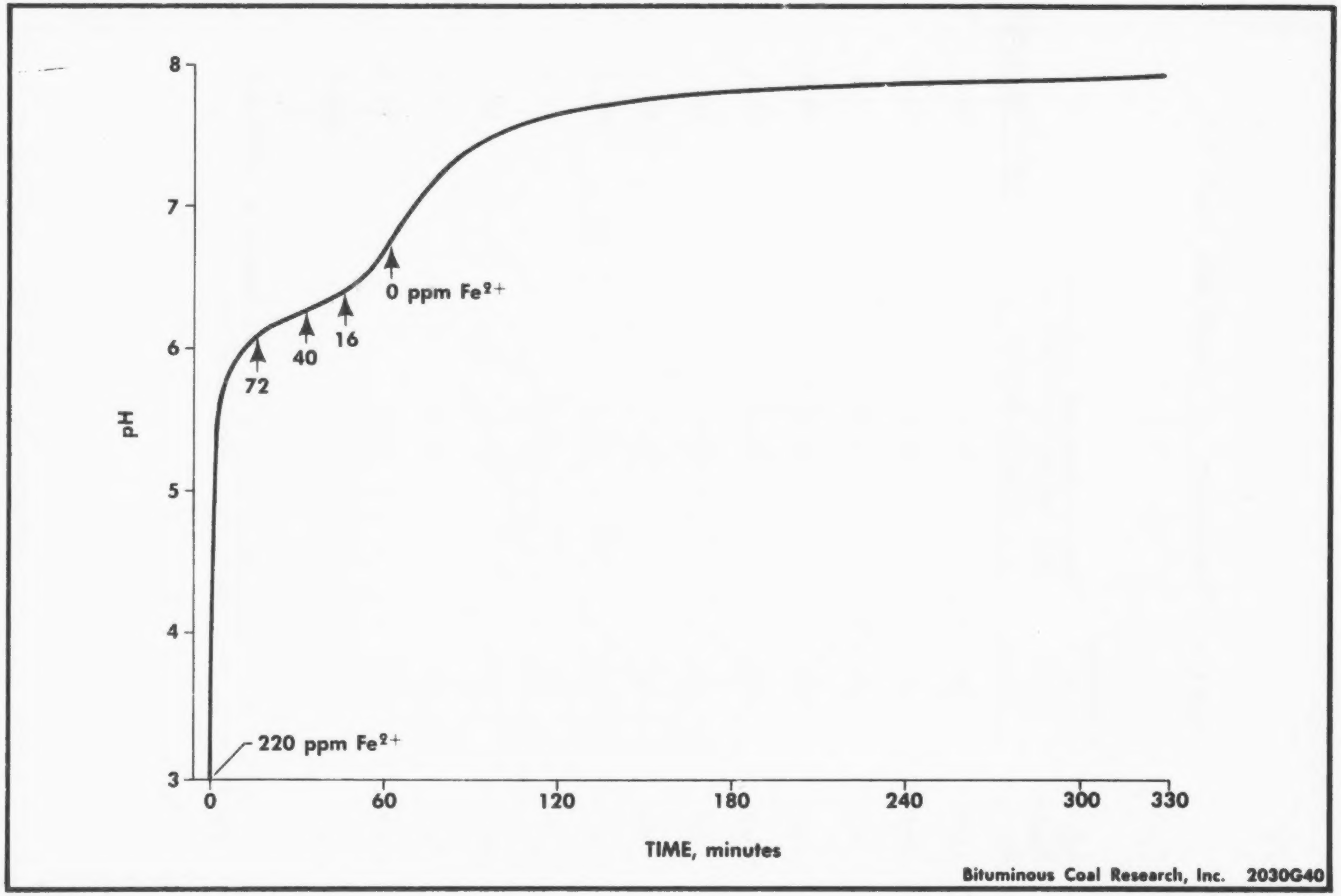

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Figure 11. Effect of Limestone No. 1809 on Synthetic Coal Mine Water

TABLE 9. "EFFICIENCY" OF LIMESTONES. CASE II+

BCR Sample No.	Relative Area Under Curve	Spectrochemical Analysis CaO Percent of (900 C) Ignited Sample	CaO + (SA x D)*
1337	30	53.0	54.7
1654	37	58.0	60.8
1461	38	4.35	7.6
1352	55	56.0	64.2
1364	62	58.0	64.1
1355	68	60.0	67.7
1362	84	55.0	62.6
2136	94	71.0	84.3
2135	95	68.0	86.9
1335	97	94.0	96.4
2145	98	92.0	97.3
1809	99	88.0	93.6
2177	100	97.0	100.0

+ Insufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added with the limestone.

* (Surface Area x Density)

The data show increasing efficiency with increasing percentage of CaO in the limestone sample. Stones with a lower percentage of CaO may be equally efficient if their specific surface area is high, as indicated in Table 9 by limestones No. 2135 and 2136.

A mathematical expression for the relationship between efficiency and some property or properties of a given limestone would be most useful as a means of evaluating limestones. Mathematical relationships considered in evaluating Case II data are listed in Table 10. The one selected [CaO + (Surface Area x Density)] has been useful to date but needs to be revised and improved as more data become available.

Case III

The data from the thirteen stones tested in Case III are listed in Table 11. A sufficient quantity of hydrogen peroxide was available to oxidize all ferrous iron present. In the case of the least efficient limestones, some ferrous iron was still present 5 minutes after addition of the stone and peroxide. No major differences between results of Case II and Case III were noted when the limestones were listed in order of increasing efficiency as determined from the area under the curves.

Case IV

Data from Case IV are given in Table 12. Some iron remained unoxidized by the least efficient stones. Few differences from Case II and Case III results were noted when the amounts of limestone were adjusted to compensate for impurities in the stones.

Limestone No. 1461, by virtue of the low CaO value, should have been the least reactive of the thirteen in this series of tests as well as in all of the past series. The area under the curve was not the least of the thirteen as one would expect. (See Tables 9, 11, and 12.) In addition, x-ray analysis (qualitative) showed only the presence of dolomite in this stone and no indication of magnesite. Clearly this sample had been mislabeled, and limestone No. 1461 is, in fact, a dolomite rather than a magnesite. Limestone No. 1462, a magnesite from Basic, Inc., Gabbs, Nevada, was then included in the Case V tests and, as expected, it was found to be the least effective neutralizing agent.

Case V

The data from testing the fourteen stones using air as the oxidant in Case V are listed in Table 13. Levels of pH attained 30, 60, and 300 minutes after addition of limestone and start of aeration are listed together with the [CaO + (Surface Area x Density)] values. These values do not vary substantially in the Case II through V experiments.

TABLE 10. MATHEMATICAL RELATIONSHIPS CONSIDERED IN EVALUATING LIMESTONES. CASE II†

BCR Sample No.	Relative Area Under Curve	CaO X SA*	CaO X SA / MgO	CaO + SA	CaO + $(SA)^2$	CaO + (SA X D**)
1337	30	32.9	0.7	53.6	53.4	54.7
1654	37	70.8	2.0	59.2	59.5	60.8
1461	38	4.8	0.1	5.4	5.6	7.6
1352	55	128.2	4.3	58.3	61.2	64.2
1364	62	123.5	37.4	60.1	62.5	64.1
1355	68	176.4	95.[illegible]	62.9	68.6	67.7
1362	84	139.2	43.[illegible]	57.5	61.4	62.6
2136	94	382.7	132.0	76.4	100.0	84.3
2135	95	488.2	191.4	75.2	119.5	86.9
1335	97	82.7	120.0	94.9	94.8	96.4
2145	98	188.6	111.6	94.0	96.2	97.3
1809	99	154.9	115.6	89.8	91.1	93.6
2177	100	113.5	97.8	98.2	98.4	100.0

† Insufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added with the limestone.

* Surface Area ** Density

TABLE 11. "EFFICIENCY" OF LIMESTONES. CASE III†

BCR Sample No.	Relative Area Under Curve	Fe^{2+}, ppm 5 Minutes After Addition of Reagents	CaO + (SA x D)*
1337	32	12	54.7
1654	36	10	60.8
1461	55	15	7.6
1364	68	2	64.1
1352	75	1	64.2
1355	75	10	67.7
1362	87	0	62.6
1335	92	0	96.4
2136	93	0	84.3
2135	95	0	86.9
2145	98	0	97.3
1809	99	0	93.6
2177	100	0	100.0

† Sufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added with the limestone.

* (Surface Area x Density)

TABLE 12. "EFFICIENCY" OF LIMESTONES. CASE IV†

BCR Sample No.	Relative Area Under Curve	Factor used in Adjusting Amount of Limestone‡	Fe^{2+}, ppm 5 Minutes after Reagent Addition	CaO + (SA x D)*
1654	32	0.95	13	60.8
1337	33	0.89	0	54.7
1461	40	0.79	14	7.6
1352	78	1.05	1	64.2
1364	87	1.64	0	64.1
1355	89	1.64	0	67.7
1335	91	1.08	0	96.4
1362	94	1.73	0	62.6
2135	96	1.44	0	86.9
2136	97	1.37	0	84.3
1809	98	1.15	0	93.6
2177	99	1.04	0	100.0
2145	100	1.09	0	97.3

† Sufficient oxidizing agent--H_2O_2, for complete oxidation of ferrous iron, added with the limestone. Amount of limestone utilized reflects compensation for impurities in the stone other than $CaCO_3$ or $MgCO_3$.

‡ $$\text{Factor} = \frac{\text{Weight of limestone needed, compensating for impurities}}{\text{Weight of limestone needed, assuming pure } CaCO_3}$$

* (Surface Area x Density)

TABLE 13. "EFFICIENCY" OF LIMESTONES. CASE V†

BCR Sample No.	Relative Area Under Curve	pH after			CaO + (SA x D)*
		30 min	60 min	300 min	
1462	30	3.6	3.9	4.9	18.0
1337	46	5.3	5.3	5.3	56.7
1461	48	5.4	5.4	5.3	56.3
1654	49	5.5	5.5	5.3	58.8
1352	49	5.5	5.5	5.4	64.2
1364	50	5.6	5.5	5.4	52.6
1355	52	5.6	5.5	5.5	71.7
1362	69	5.7	5.6	7.4	76.6
2136	87	5.7	5.9	7.8	85.2
2135	87	5.8	5.9	7.8	85.0
1335	94	5.9	7.4	7.9	96.4
2145	95	6.0	7.8	7.9	95.3
1809	96	6.1	7.8	7.9	94.6
2177	100	7.6	8.0	8.0	98.0

† Sufficient oxidizing agent--air, for complete oxidation of ferrous iron, introduced at the same time as limestone addition and continued throughout the reaction period.

* (Surface Area x Density)

The experimental conditions observed under Case V are recommended as the best method to date of evaluating limestones as neutralizing agents for coal mine water. These conditions are: addition of 325 x 400 mesh limestone and air to a solution of synthetic coal mine water containing 200 to 250 ppm of Fe^{2+} added as ferrous sulfate and having the pH adjusted to 3.0 with sulfuric acid; stirring continuously for a 5.5 hour period and recording the changes in pH with time. The amount of limestone should be twice the stoichiometric amount based on the acidity of the synthetic coal mine water and based on the assumption that the stone contained pure $CaCO_3$. Air should be bubbled into the solution through a fritted glass disk at the bottom of the container throughout the reaction at a rate of 2500 ml/min.

A composite graph of all results from the past tests should be used to judge the results of this experiment. Such a composite is presented in Figure 12. The curve from an effective limestone would fall into area A on Figure 12, while curves from ineffective limestones would resemble those in areas B or C.

There was no essential difference in the results of the Case II through Case V experiments; therefore, air was selected as the oxidant. Air is the cheapest oxidant and is therefore used in coal mine water treatment operations. There was not too much difference in the results of the Case IV experiments when a compensation was made for impurities in the limestone. Therefore, in the method being recommended, limestones are assumed to be pure $CaCO_3$. Ultimately only two categories of limestones are reasonable--those stones which are effective neutralizing agents and those which are not--in terms of their ability to effect a change in pH. For coal mine water treatment, a time factor must be considered along with the change in pH. As a result of the evaluation of the 14 limestones, the effective stones are No. 1335, 1809, 2135, 2136, 2145, and 2177. Those stones which are judged to be ineffective are No. 1337, 1352, 1355, 1362, 1364, 1461, 1462, and 1654.

In general, based on the five series of experiments, magnesites are the least effective neutralizing agents, followed closely by dolomitic stones. Stones approaching pure $CaCO_3$ are the most effective neutralizing agents. Stones having a relatively low calcium content, but a calcite structure and a high surface area, are equally effective neutralizing agents.

The effectiveness of limestones as neutralizing agents for coal mine waters can be enhanced by reducing the particle size of the stone.

Batch-scale Neutralization of Actual Coal Mine Waters

Although four actual coal mine waters were initially chosen for batch-scale limestone neutralization studies, exploratory neutralization tests were performed on only three of these waters, namely, South Greensburg, Keystone, and Tarrs. It was felt that any conditions

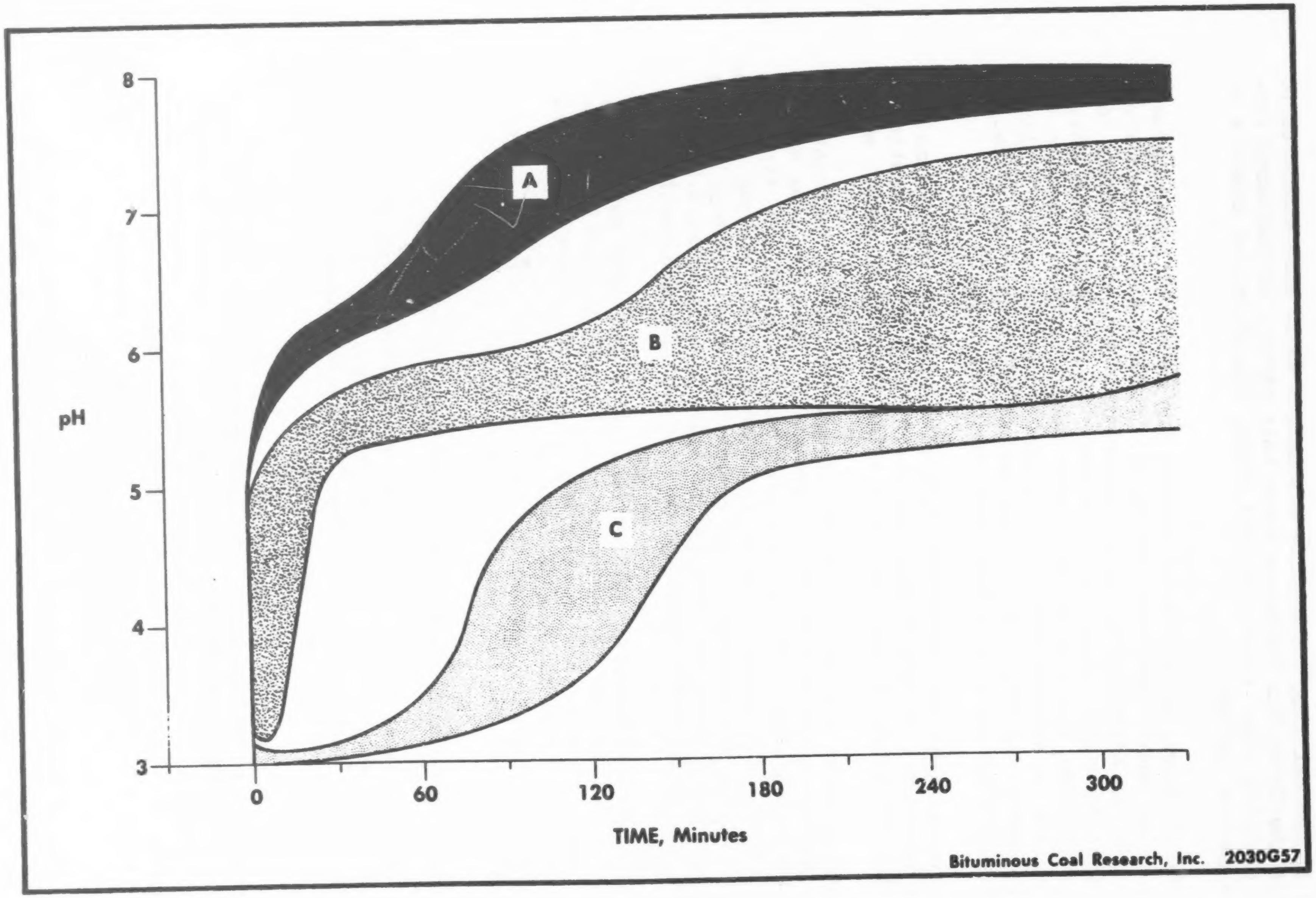

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Figure 12. Model Curve for Judging Effectiveness of Limestones

employed in neutralizing these three discharges would also enable us to neutralize the Thorn Run discharge since this particular discharge contains essentially only ferric iron and would, therefore, be amenable to limestone neutralization.

Figure 13 shows the effect of varying the amount of limestone used in neutralizing South Greensburg discharge. Reduction in ferrous iron concentration was accomplished in all experiments but most rapidly in that one with an excess amount of limestone. It may be assumed that, allowing sufficient time, there would have been a further reduction in iron in the one experiment with the stoichiometric (1X) amount of limestone. In commercial practice a slight excess of stone could probably be tolerated economically to obtain more rapid reaction.

Surprisingly, in the experiment with five times the stoichiometric amount of limestone, no improvement was observed in the rate at which ferrous iron was oxidized over that with twice the stoichiometric amount.

Figure 14 shows the results of two experiments using the Keystone discharge and twice the stoichiometric amount of limestone. One experiment was conducted with aeration, the other without aeration. Figure 15 shows the effect of aeration on pH of the same systems. Ferrous iron can be oxidized during neutralization of Keystone coal mine drainage without aeration, but about twice the time is necessary to remove the Fe^{2+}. Maximum pH and minimum Fe^{2+} values occur at about the same period.

In the last experiment of this series, Tarrs coal mine drainage was treated with twice the stoichiometric amount of No. 1809 limestone, 325 x 400 mesh. Stirring and aeration for 90 minutes, however, failed to reduce the Fe^{2+} concentration or to increase the pH above 6.7. Aeration and stirring were resumed the next day for 30 minutes. This effected oxidation of the Fe^{2+} and an increase of the pH to 7.

Tests on Actual Coal Mine Water under Standardized Conditions

From data obtained in the exploratory tests above, a standardized set of conditions was selected for batch-scale limestone neutralization of the four actual coal mine waters (See "Batch-scale Neutralization of Actual Coal Mine Waters," under Section 3).

The resultant data are summarized in Tables 14, 15, 16, and 17. Complete analyses of the waters as received are given in column A; complete analyses of these waters after treatment for 90 minutes in column B; after treatment for 90 minutes and allowing to stand overnight, in column C; and, after treatment for 90 minutes, allowing to stand overnight, and being stirred and aerated an additional 30 minutes in column D.

Treatment of South Greensburg coal mine drainage (Table 14) was accomplished quite effectively. Iron content and acidity were reduced to low levels after standing overnight (column C). Little difference

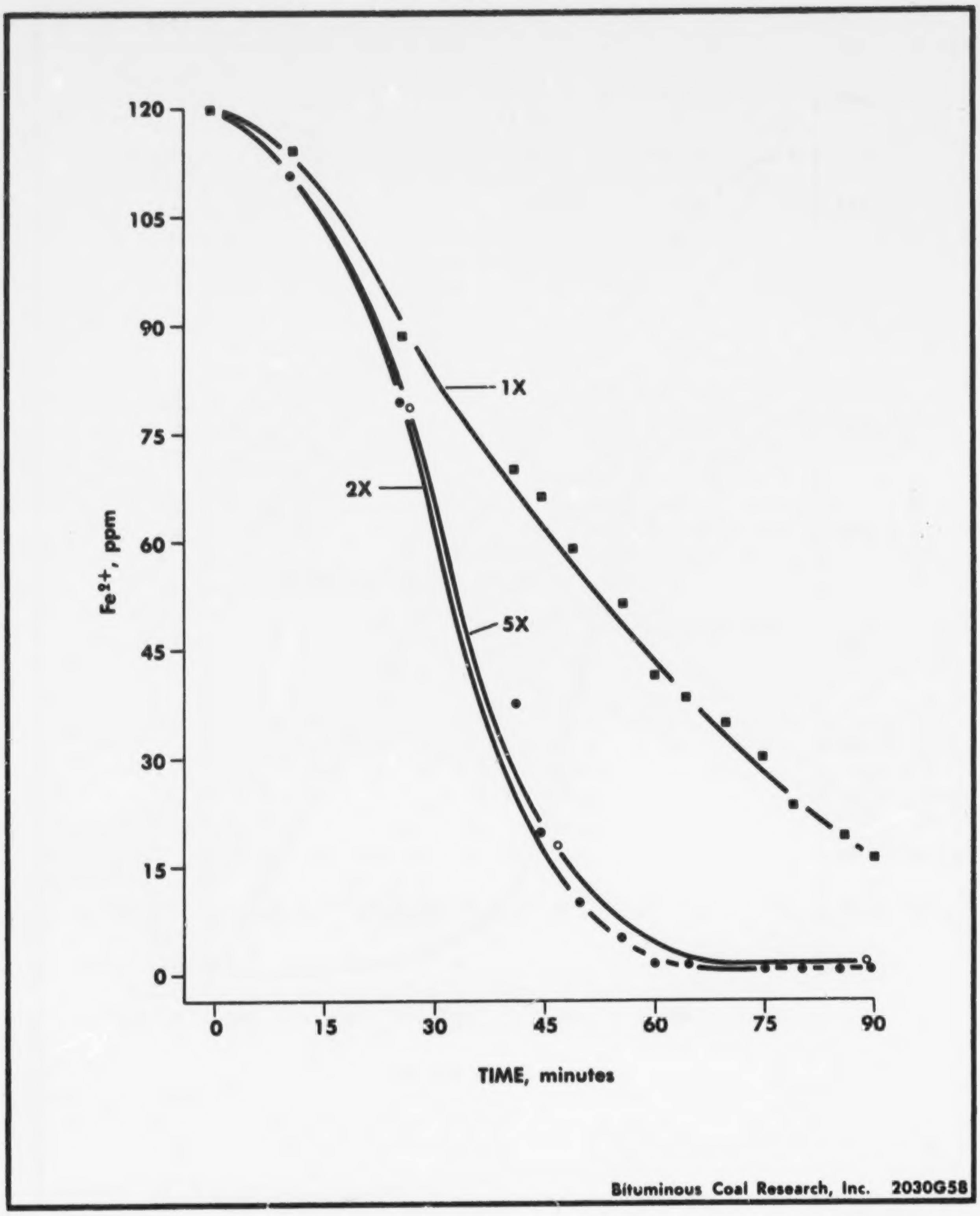

Figure 13. Neutralization of South Greensburg Coal Mine Drainage—Effect of Amount of No. 1809 Limestone on Fe^{2+}

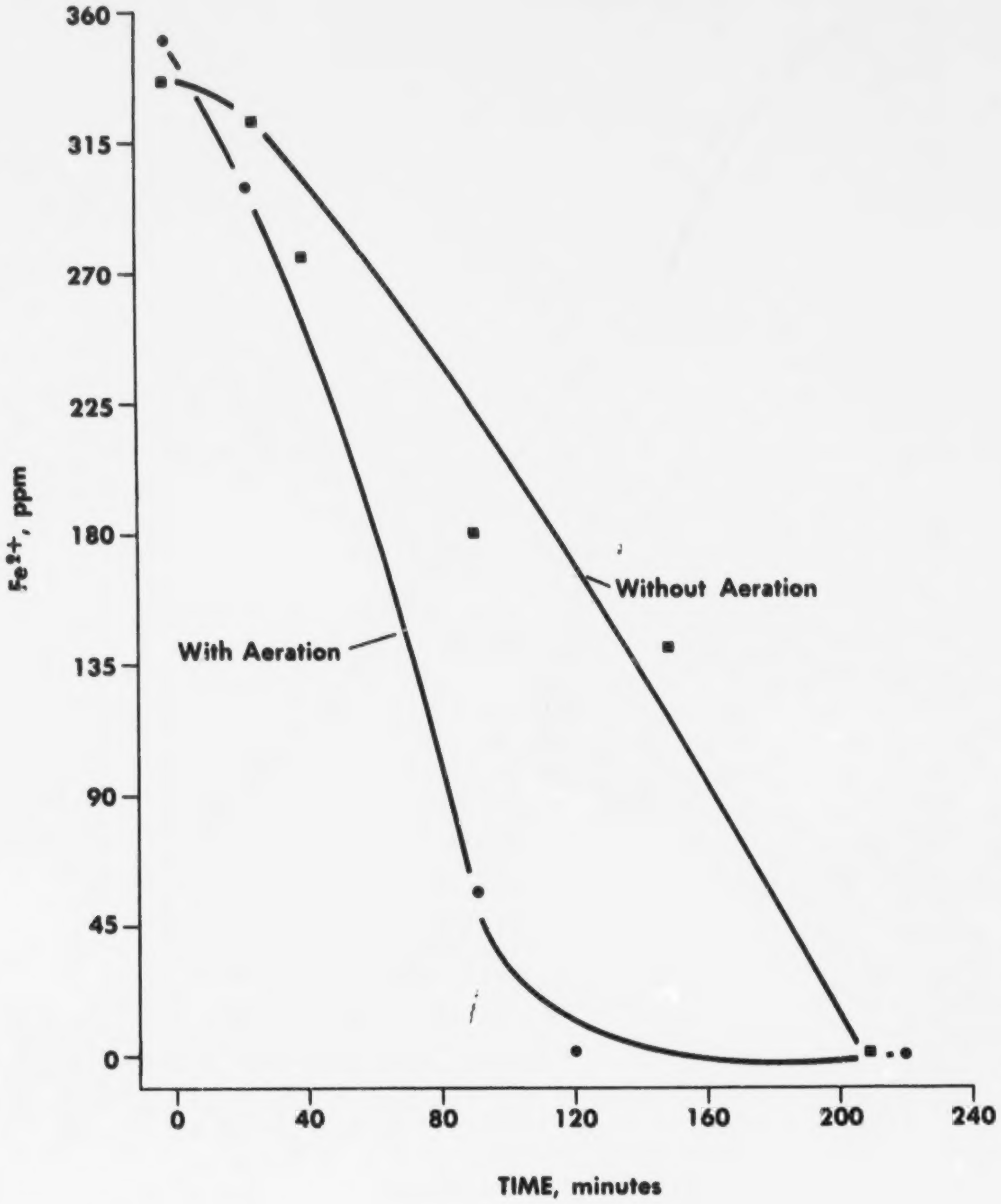

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Figure 14. Neutralization of Keystone Coal Mine Drainage with No. 1809 Limestone—Effect of Aeration on Fe^{2+}

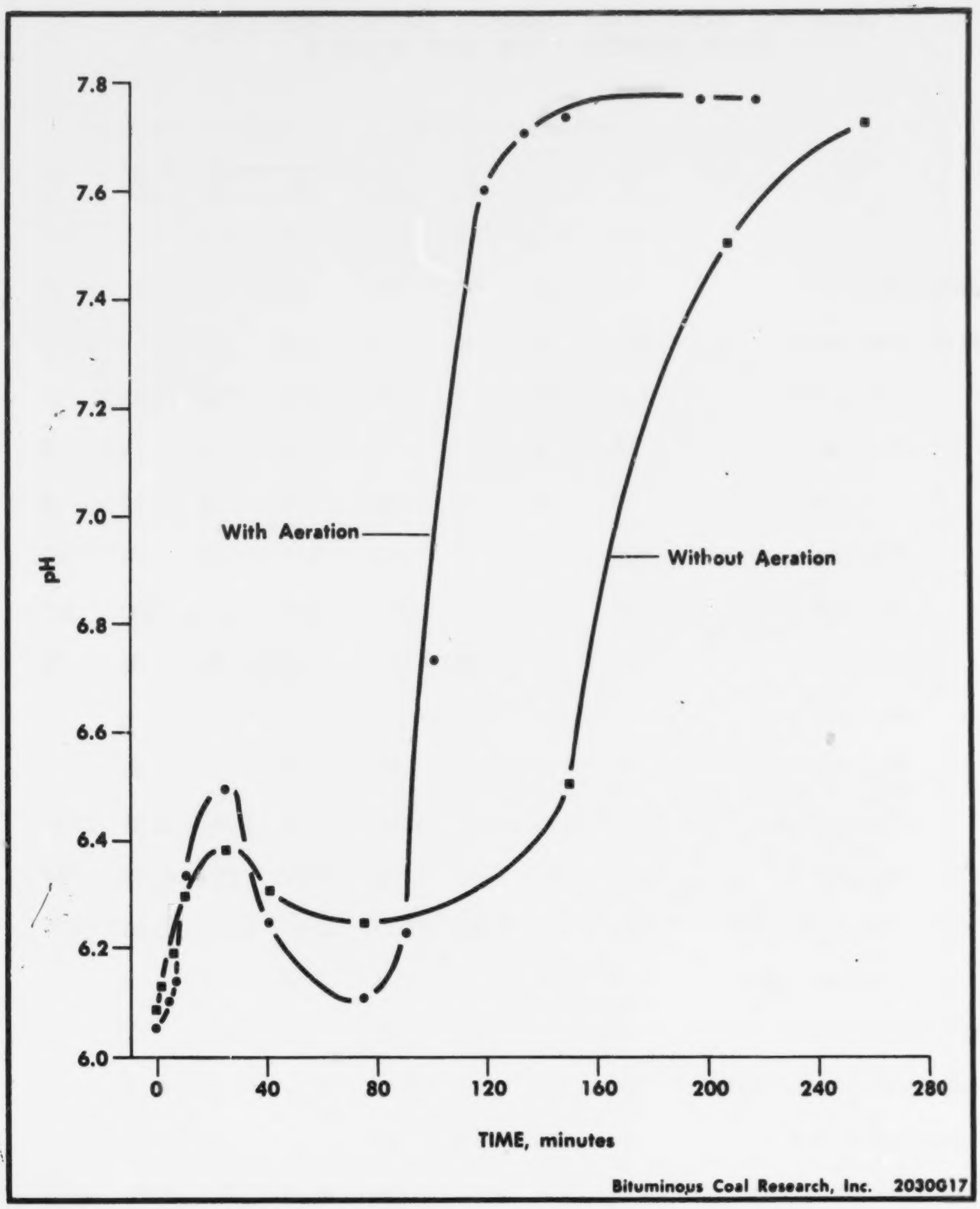

Figure 15. Neutralization of Keystone Coal Mine Drainage with No. 1809 Limestone—Effect of Aeration on pH

TABLE 14. BATCH-SCALE LIMESTONE NEUTRALIZATION OF SOUTH GREENSBURG COAL MINE DRAINAGE

	Initial Reaction at 18 C				Initial Reaction at 22 C			
	A	B	C	D	A	B	C	D
pH	5.1	6.4	6.8	7.6	4.6	6.4	6.5	7.6
Temperature, °C	18	21	20	20	22	22	20	20
Acidity, ppm $CaCO_3$	220	60	18	0	260	53	4	0
Fe^{2+}, ppm	111	24	3	<1	106	24	<1	<1
Si, ppm	14	6	4	4	12	6	4	4
Al, ppm	7	<2	<2	<2	6	2	<2	<2
Fe, ppm	109	20	4	<4	111	24	<4	<4
Ca, ppm	219	300	355	360	205	290	320	325
Mg, ppm	82	80	80	83	82	82	82	84
Mn, ppm	4	4	4	4	3	3	3	3
Na, ppm	73	77	93	87	58	60	64	74
SO_4^{2-}, ppm	1099	1098	1118	1141	1099	1093	1131	1131
Eh, mv	+412	+347	+392	+472	+452	+352	+352	+447
Conductivity, μmhos/cm	2060	2080	2090	2140	1950	2080	2160	2170
Dissolved Oxygen, ppm	5	8	5	8	6	7	8	8
Turbidity, JTU	5	8	<1	<1	8	<1	<1	1
Electrophoretic Mobility	--	+1.0	+0.6	+0.5	--	+0.7	+0.4	+0.4
Zeta Potential, mv	--	+14	+8	+7	--	+9	+5	+5
Dissolved Solids, ppm	1900	1700	2150	2030	2010	1660	2080	2010

A = Raw mine water
B = A, after treatment for 90 minutes
C = B, allowed to stand overnight
D = C, stirred and aerated an additional 30 minutes

TABLE 15. BATCH-SCALE LIMESTONE NEUTRALIZATION OF KEYSTONE COAL MINE DRAINAGE

	Initial Reaction at 18 C				Initial Reaction at 22 C			
	A	B	C	D	A	B	C	D
pH	6.3	6.2	6.6	7.7	6.3	6.3	6.8	7.7
Temperature, °C	18	22	21	22	22	23	21	22
Acidity, ppm $CaCO_3$	342	38	13	8	342	34	0	0
Fe^{2+}, ppm	325	14	0	0	325	3	0	0
Si, ppm	7	3	2	1	7	2	1	1
Al, ppm	<2	<2	2	2	<2	2	2	2
Fe, ppm	330	13	<4	4	330	6	<4	<4
Ca, ppm	255	355	380	380	255	385	400	390
Mg, ppm	119	114	115	115	119	120	120	120
Mn, ppm	5	4	4	4	5	5	4	4
Na, ppm	1070	1110	1270	1250	1070	1230	1230	1200
SO_4^{2-}, ppm	3598	3590	3667	3673	3598	3570	3640	3580
Eh, mv	+232	+322	+367	+397	+232	+327	+417	+417
Conductivity, μmhos/cm	6510	6430	6460	6480	6510	6440	6480	6480
Dissolved oxygen, ppm	7	8	7	8	7	8	8	8
Turbidity, JTU	38	1	1	1	38	1	5	1
Electrophoretic Mobility	--	+1.1	+1.1	+1.1	--	+1.1	+1.1	+1.0
Zeta Potential, mv	--	+14	+14	+14	--	+15	+16	+13
Dissolved solids, ppm	5810	5130	5710	5940	5810	5290	5780	5590

A = Raw mine water
B = A, after treatment for 90 minutes
C = B, allowed to stand overnight
D = C, stirred and aerated an additional 30 minutes

TABLE 16. BATCH-SCALE LIMESTONE NEUTRALIZATION OF TARRS COAL MINE DRAINAGE

	Initial Reaction at 18 C				Initial Reaction at 22 C			
	A	B	C	D	A	B	C	D
pH	3.1	6.6	6.5	6.9	3.0	6.1	6.4	7.0
Temperature, °C	18	21	20	20	22	22	20	20
Acidity, ppm $CaCO_3$	673	100	66	25	673	95	75	40
Fe^{2+}, ppm	84	44	25	6	84	34	20	4
Si, ppm	45	17	12	9	45	16	12	9
Al, ppm	62	<2	<2	<2	62	<2	<2	<2
Fe, ppm	122	44	22	8	122	36	22	7
Ca, ppm	237	500	500	510	237	470	500	520
Mg, ppm	94	94	90	90	94	92	94	94
Mn, ppm	5	5	5	5	5	5	5	5
Na, ppm	<30	<30	<30	<30	<30	<30	<30	<30
SO_4^{2-}, ppm	1441	1422	1468	1472	1441	1440	1485	1484
Eh, mv	+662	+392	+367	+472	+662	+382	+372	+482
Conductivity, μmhos/cm	2170	2170	2150	2160	2170	2170	2150	2160
Dissolved oxygen, ppm	8	8	8	7	8	8	7	8
Turbidity, JTU	4	1	1	1	4	1	1	1
Electrophoretic mobility	--	+0.6	+0.7	+0.5	--	+0.7	+0.6	+0.5
Zeta potential, mv	--	+8	+9	+7	--	+9	+8	+7
Dissolved solids, ppm	2460	2200	2330	2160	2460	2170	2120	2540

A = Raw mine water
B = A, after treatment for 90 minutes
C = B, allowed to stand overnight
D = C, stirred and aerated an additional 30 minutes

TABLE 17. BATCH-SCALE LIMESTONE NEUTRALIZATION OF THORN RUN COAL MINE DRAINAGE

	Initial Reaction at 18 C				Initial Reaction at 22 C			
	A	B	C	D	A	B	C	D
pH	3.2	7.2	6.3	7.6	3.2	7.3	6.6	7.5
Temperature, °C	18	20	20	20	22	22	20	20
Acidity, ppm $CaCO_3$	478	16	9	6	478	18	9	0
Fe^{2+}, ppm	18	<1	<1	<1	18	<1	<1	<1
Si, ppm	20	3	2	1	20	3	2	1
Al, ppm	51	3	<2	<2	51	2	2	2
Fe, ppm	69	<4	<4	<4	69	<4	<4	<4
Ca, ppm	250	490	480	470	250	395	410	430
Mg, ppm	66	68	67	68	66	67	69	71
Mn, ppm	13	12	12	12	13	11	11	11
Na, ppm	30	30	30	30	30	25	25	30
SO_4^{2-}, ppm	1182	1191	1118	1197	1182	1200	1224	1198
Eh, mv	+697	+442	+467	+462	+697	+522	+462	+457
Conductivity, μmhos/cm	2140	2160	2150	2150	2140	2140	2140	2160
Dissolved oxygen, ppm	13	8	8	9	13	9	8	8
Turbidity, JTU	10	1	1	1	10	1	1	1
Electrophoretic mobility	--	+0.75	+0.5	+0.4	--	+0.6	+0.5	+0.6
Zeta potential, mv	--	+10	+7	+5	--	+8	+7	+8
Dissolved solids, ppm	1900	2200	2200	2180	1900	2110	2020	2020

A = Raw mine water
B = A, after treatment for 90 minutes
C = B, allowed to stand overnight
D = C, stirred and aerated an additional 30 minutes

was noted between initial reaction at 18 C and 22 C (column B).

Treatment of Keystone coal mine drainage (Table 15) proceeded effectively with only minor differences between reaction at 18 C and 22 C. Again iron content and acidity were reduced to low levels after the sample was allowed to stand overnight.

Treatment of Tarrs discharge (Table 16) proceeded slowly. Acidity and iron content were not lowered substantially even after the sample was allowed to stand overnight. Only after stirring and aeration for an additional 30 minutes were the iron content and acidity further reduced. Aluminum was also removed, however, this treatment did not affect manganese concentration.

The most effective treatment occurred with Thorn Run discharge (Table 17). Low levels of acidity and iron content were observed after treatment for only 90 minutes (column B).

In all cases, an increase in concentration of Ca, and therefore hardness, was noted as a result of the limestone neutralization. Dissolved oxygen usually attained a final value of 8 ppm in the treated water. No significant increase in dissolved solids or conductivity was noted.

Electrostatic charge on the sludge particles as reflected by electrophoretic mobility and zeta potential, was reduced on standing (columns B, C, and D) in most cases; this should mean a more rapid settling of sludge.

Turbidity was reduced to 1 JTU, the value also obtained on tap water.

The four actual mine waters have been treated successfully but with varying degrees of difficulty. These batch-scale tests point out the need for a general set of conditions for neutralization with limestone, which can be varied as required by the characteristics of the individual water.

Oxidation of Ferrous Iron

Ferrous iron in some actual coal mine waters is not oxidized readily by aeration alone. (See Table 16.) A method to enhance this oxidation in the limestone neutralization process is needed. The use of carbon catalysts to promote the air oxidation of Fe^{2+} in an acid medium (12, 13) and the use of activated carbon alone as a solid catalyst (14, 15) have been studied by others. However, so far as is known, no work has been done on the use of such carbons for the oxidation of Fe^{2+} in coal mine water. This study was undertaken to test the applicability of carbon catalysts described in the literature to coal mine water treatment.

Catalyst Preparation

Initially these catalysts were prepared from a number of materials. Preliminary studies were conducted to evaluate a variety of carbon catalyst preparation schemes. Carbons, produced from coconut char, foundry coke, and hardwood sawdust, were subjected to activation by air and by chemical action. Most carbons prepared in this manner had high catalytic activity but lacked the desired mechanical strength. The general procedure for preparing an active carbon was both laborious and complex. (See Experimental Section.)

Four typical prepared materials were selected for study. Carbon 334-92-2 was made from Sewell coal devolatilized at 800 C for 45 minutes, activated at 300-375 C for 1 hour and calcined at 750 C for 3.5 hours. Carbon 334-92-3 was also made from Sewell coal devolatilized at 510 C for 2.5 hours, activated at 375 C for 1 hour and calcined at 950 C for 1 hour. The calcination at 950 C was accomplished in N_2 saturated with water at 90 C, essentially a steam activation step. Carbon 334-92-1 was a steam-activated coke from Rochester and Pittsburgh Coal Company which was further steam activated in our laboratories by heating at 950 C for 1 hour in N_2 saturated with water at 90 C. The fourth carbon, 334-75-2, was made from Sewell coal and devolatilized at 700 C for 15 minutes, activated at 480 C for 90 minutes, and calcined at 800 C for 3 hours.

Testing Prepared Activated Carbons

The four carbons were evaluated in the standard test. Data from 334-92-1, 334-92-2, and 334-92-3 are listed in Table 18. Percent Fe^{2+} converted is adequate in all but 334-92-1. The life of the catalyst was examined using the fourth carbon, 334-72-2 with only 4 g of carbon being used with 50 ml portions of test solution. Aeration at 400 ml/min was carried out for 15-minute cycles. The carbon was filtered off with no washing after each cycle. The data are presented in Table 19. A constant level of activity was maintained throughout the test. The results show that the catalyst maintained activity at low pH for 20 cycles. In a coal mine drainage treatment process, the life of the carbon must be long and mechanical losses low. These tests indicate that the catalyst life is at least 300 minutes without being regenerated.

Testing Commercially Available Activated Carbons with Synthetic Coal Mine Water

Testing of commercially available, coal-derived activated carbons was initiated since preparing the carbon from coal in our laboratories left little time for actual testing of the materials made. In the preliminary experiments, using limestone together with the carbon in the test solution during aeration, the carbon soon became coated with precipitated oxidation products; for this reason, use of the

TABLE 18. EVALUATION OF PREPARED CARBON AS CATALYSTS FOR Fe^{2+} OXIDATION

Carbon Sample Number	Air Rate, ml/min	Duration of Test, min	Percent Fe^{2+} Converted					
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
334-92-1	400	15	33	32	34	36	32	--
334-92-2	400	15	28	39	47	50	58	55
334-92-3	400	15	83	76	76	--	--	--

TABLE 19. EVALUATION OF LIFE OF A PREPARED ACTIVATED CARBON CATALYST

Cycle No.	Percent Fe^{2+} Oxidized	Cycle No.	Percent Fe^{2+} Oxidized
1	47	11	56
2	47	12	53
3	49	13	53
4	50	14	55
5	52	15	60
6	51	16	57
7	51	17	56
8	58	18	55
9	56	19	56
10	55	20	54

combination of carbon and limestone was discontinued, even though the rate of oxidation was increased satisfactorily.

Early experiments with commercially available activated carbons were also concerned with testing a number of coal-derived carbons and varying the quantity of carbon and duration of the test (cycle). The carbons were either used "as is" out of the container or were subjected to steam activation by heating at 950 C for 1 hour in an atmosphere of N_2 saturated with water at 90 C. An aeration rate of 400 ml/min was employed in all of these tests. Results of these experiments are listed in Table 20. No satisfactory increase in the rate of oxidation with the carbon present was noted in the first 15-minute cycle; the rate of oxidation did increase with increasing number of cycles both in cases where the carbon had been steam activated (Sample No. 334-97-15A and Sample No. 334-96-14A) and when used as received (Sample No. 334-96-13C).

To examine the effect of increasing the number of cycles on the oxidation rate, Nuchar WV-W was used as received in the standard test. The data are listed in Table 21. After a few unproductive cycles, a rate of oxidation between 60 and 80 percent was attained in a 60-minute cycle. The catalyst maintained this activity for 24 cycles, a total of 22-3/4 hours. When the duration of the cycle was reduced to 30 minutes (cycle 21) or 15 minutes (cycle 22), there was a corresponding decrease in percent Fe^{2+} oxidized.

It has been suggested that a build-up of bacteria during the first few unproductive cycles is responsible for the increased catalytic activity. While there is no direct evidence against such a build-up, this mechanism does not seem likely based on the immediate catalytic activity exhibited by the steam activated material (See Table 20, Carbon Sample No. 334-96-14C and 334-97-16).

It was thought that the difficulty in limestone treatment of Tarrs discharge, as shown in Table 16, might have been due to the presence of aluminum as well as ferrous iron in this water. To examine the effect of aluminum, the following experiment was conducted. Approximately 150 ppm, as $Al_2(SO_4)_3 \, 18 \, H_2O$, was added to the test solution. The 1-hour reaction showed no diminishing of efficiency; if anything, the efficiency was slightly increased.

In summary, the commercially available activated carbons are effective catalysts, either (a) after further steam activation or (b) after merely undergoing a few relatively unproductive cycles. A cycle of 60 minutes duration is necessary to accomplish 60 to 80 percent oxidation of ferrous iron in synthetic coal mine water at pH 3.0.

Testing Commercially Available Activated Carbons with Actual Coal Mine Water

Tarrs discharge, an actual coal mine water, was then tested. This

TABLE 20. EVALUATION OF COMMERCIALLY AVAILABLE ACTIVATED CARBONS FOR Fe^{2+} OXIDATION

Carbon Sample No. 334-	Carbon Description	Quantity of Carbon, g/1	Duration of Test, min	Percent Fe^{2+} Oxidized Cycle 1	Cycle 2	Cycle 3	Cycle 4
Control		0	60	2	2	2	2
	Pittsburgh Activated Carbon Company						
92- 4	OL, as received	80	15	34	18	14	--
92- 5	CAL, as received	80	15	46	22	13	--
92- 6	SGL, as received	80	15	32	22	--	--
94-12	BPL, as received	80	15	21	16	--	--
97-15A	BPL, steam activated	107	15	33	63	79	91
97-15B	BPL, steam activated	107	30	44	69	--	--
	West Virginia Pulp and Paper Company						
93- 7	Nuchar WV-G, as received	80	15	16	20	--	--
93- 9	Nuchar C-115-N, as received	80	15	22	20	--	--
93-10	Nuchar C-190-N, as received	80	15	27	24	--	--
93-11	Aqua Nuchar A, as received	80	15	22	16	--	--
96-13A	Nuchar WV-W, as received	160	15	20	--	--	--
96-13B	Nuchar WV-W, as received	160	30	15	--	--	--
96-13C	Nuchar WV-W, as received	160	60	50	38	56	68
96-14A	Nuchar WV-W, steam activated	160	15	46	66	79	86
96-14B	Nuchar WV-W, steam activated	160	30	79	93	--	--
96-14C	Nuchar WV-W, steam activated	160	60	85	--	--	--
97-16	Nuchar WV-W, steam activated	107	60	84	--	--	--

TABLE 21. EVALUATION OF LIFE OF COMMERCIALLY AVAILABLE ACTIVATED CARBON CATALYST

Cycle No.	Reaction Time, min	Percent Fe^{3+} Oxidized
1	60	2
2	60	34
3	60	50
4	60	60
5	60	61
6	60	52
7	60	66
8	60	70
9	60	73
10	60	74
11	60	65
12	60	73
13	60	76
14	60	76
15	60	77
16	60	75
17	60	67
18	60	72
19	60	73
20	60	73
21	30	61
22	15	40
23	60	62
24	60	68

water, containing 52 ppm of Fe^{2+} at pH 3.10, was aerated at a rate of 400 ml/min in the presence of 16 g of activated carbon (Nuchar WV-W), and also with no carbon present. (See Figure 16.) The rate of ferrous iron oxidation was increased significantly by the presence of the activated carbon. After 60 minutes, pH decreased to 2.89. At least in this particular coal mine water, oxidation of 80 percent of the ferrous iron can be accomplished in 15 minutes without first raising the pH by the addition of a neutralizing agent. Further, the low pH at the end of the oxidation reaction ensures against the iron precipitating on the carbon and rendering it inactive and necessitating constant backwashing.

Testing Other Materials

Materials other than activated carbon were also tested in the same manner as the carbons using synthetic coal mine water. In all cases, the aeration rate was 400 ml/min. Table 22 lists these materials, showing their effect on ferrous iron oxidation and terminal pH achieved. (The test solution in these cases contained 212 ppm Fe^{2+} as ferrous sulfate adjusted to pH 3.0 with sulfuric acid.) These materials, some of which have a surface area as great as carbon, accelerated the rate of oxidation only when they also effected an increase in pH. It is felt that the increase in pH was responsible for the increased rate of oxidation rather than any mechanism similar to that of the carbon. Stumm and Lee (16) report a hundredfold increase in the rate of oxidation of ferrous iron per unit increase in pH.

No insight regarding the mechansim of this carbon catalysis of ferrous iron oxidation or the increase in catalytic activity after the first few unproductive cycles was obtained by (a) Soxhlet extraction and analysis of the filtrate, (b) pyrolysis of the carbon and analysis of the resultant gases, or (c) x-ray analysis of the commercially available, coal-derived carbons both as received and when good catalytic activity was attained.

The surface of activated carbon has a variety of organic functional groups containing oxygen and hydrogen. Activated carbon has been described as a disordered agglomerate of layers of large polynuclear benzenoid hydrocarbons. Oxygen, which is adsorbed in amounts proportional to the amount of oxygen in solution, probably reacts as a diradical —O—O— (17), in conjunction with hydrogen ions, to extract electrons from the adsorbed ferrous ions.(13)

Non-oxidative Neutralization and Addition of Coagulant Aids

Electrophoretic mobility measurements have shown that particles of freshly prepared ferrous hydroxide formed by the non-oxidative neutralization of synthetic coal mine water have an electrostatic charge of +9 to +16 millivolts. Reduction of this charge to a minimum will reduce the forces of mutual repulsion; this can be accomplished by the addition of specific amounts of an anionic electrolyte or polyelectrolyte. Gentle agitation at this point will then increase the number of colli-

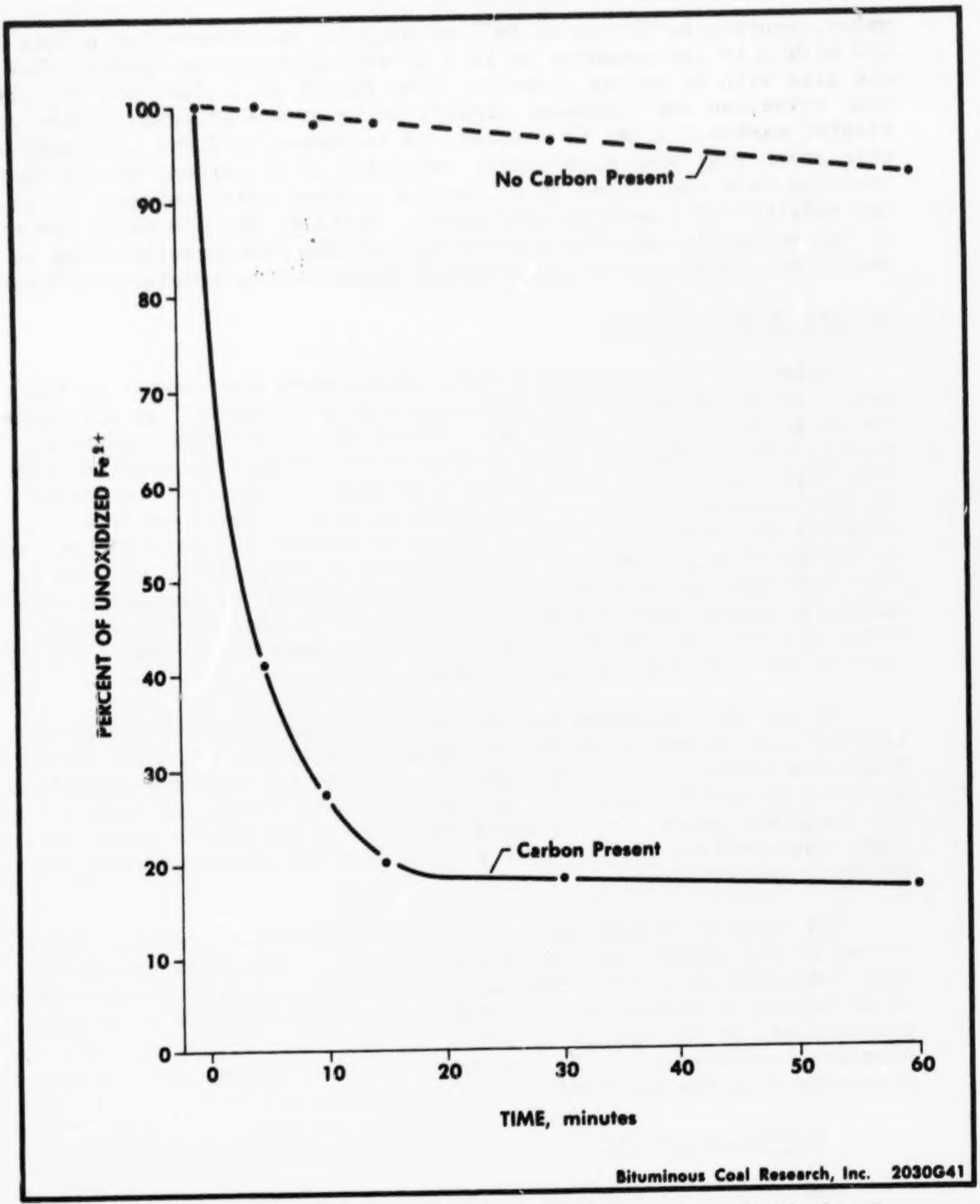

Figure 16. Effect of Activated Carbon on Ferrous Iron Oxidation Tarrs Coal Mine Discharge

TABLE 22. EFFECT OF MATERIALS OTHER THAN CARBON ON FERROUS IRON OXIDATION

Material	Description	Terminal pH	Percent Fe^{2+} Oxidized
Al_2O_3	Minus 200 mesh	3.2	5
Clay No. 1	Kaolin, minus 200 mesh	3.1	15
Clay No. 2	Bentonite, minus 200 mesh	6.2	69
Clay No. 3	Attapulgite, minus 200 mesh	5.6	61
Clay No. 3	Same as above, but fired at 1400° F for 10 min	3.3	21
Clay, M and D	Ball clay, mostly kaolinite	4.5	73
Fly Ash	Similar to coal ash but not completely burned, minus 400 mesh	5.9	77
Fly Ash	Same as above, sintered, 1/2-inch x 1/2-inch	5.3	0
Molecular Sieve, 4A	Hewlett-Packard, 60 x 80 mesh	10.0	82
Molecular Sieve, 5A	F and M Scientific, 30 x 60 mesh	6.4	78
Molecular Sieve, 13X	F and M Scientific, 30 x 60 mesh	7.3	89
White Sand	Common, hardware store variety	3.2	3
Sludge	From limestone neutralization of South Greensburg coal mine drainage	6.6	73

sions so that the short range van der Waals' forces can furnish the attraction required to cause coagulation and thus markedly increase the settling rate. The electrophoretic mobility studies were undertaken to examine the effect of various coagulant aids (electrolytes, polyelectrolytes, and inert solids) on the electrostatic charge of ferrous hydroxide particles and to apply the information gained toward improved settling of these particles.

Electrophoretic Mobility Studies

The effect of coagulant aids on the electrostatic charge (zeta potential) on particles in suspension is illustrated in Figure 17. Addition of < 1 ppm of some types of coagulant aids will achieve the isoelectric point (curve A); an excess amount of this same type is actually detrimental since it produces a more dispersed suspension. However, the isoelectric point is never achieved with other types of coagulant aids (curve B). It is at or near the isoelectric point, where the forces of mutual repulsion are minimized, the coagulation and faster settling can occur. Furthermore, high molecular weight, viscous polymers introduced at this point are adsorbed on the suspended solids, thereby producing stable flocs and improving the settling rate of the solid particles. Some polymers act as electrolytes as well, and thus fill the dual role by both minimizing the charge on the particles and enhancing the formation of stable flocs.

Effect of Coagulant Aids Alone

Various types of coagulant aids were first tested to establish their effectiveness in minimizing the electrostatic charge on the ferrous hydroxide particles. This effectiveness was indicated by the amount of aid required to reduce the zeta potential to zero. Types of aids tested included: (a) anionic polyelectrolytes, (b) anionic electrolytes, and (c) inert solids.

Altogether, 11 electrolytes and polyelectrolytes and 3 inert solids were tested. A description of the materials tested is given in Table 23 together with the results obtained.

The first set of tests (Figure 18) shows the effect of 3 siliceous materials, all of which can be considered anionic polyelectrolytes, on the zeta potential of ferrous hydroxide. In only one case, with solution No. 24, was the isoelectric point achieved; even here, charge reversal was not achieved.

In the second set, three other anionic materials were tested (Figure 19). The isoelectric point was reached with the anionic electrolyte, $Na_4P_2O_7$, at a concentration of 100 ppm. The isoelectric point was attained by the addition of approximately 75 ppm of Calgon C-55, a mixture of materials recommended for silt control by Calgon Corporation. This mixture appears to be both anionic and polymeric. Addition of Calgon C-55 in concentrations greater than 75 ppm changes the zeta po-

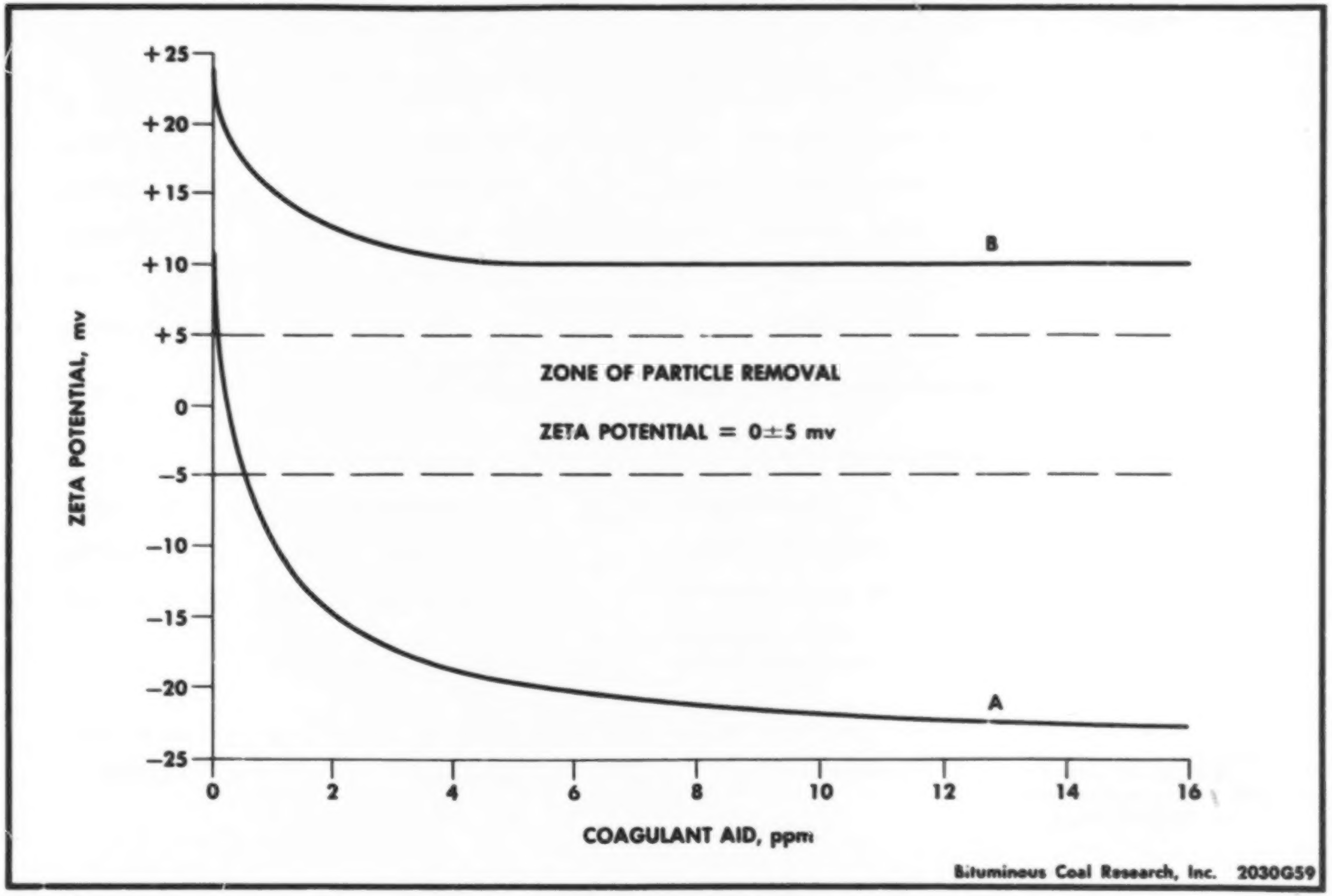

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Figure 17. Effect of Coagulant Aids on Zeta Potential

TABLE 23. EFFECT OF COAGULANT AIDS ON $Fe(OH)_3$

Additive	Source	Description	Concentration at Isoelectric Point, ppm Added to $Fe(OH)_3$
Ludox HS-40	E. I. duPont de Nemours & Co.	Sodium stabilized colloidal silica	*
Ludox AS	E. I. duPont de Nemours & Co.	Ammonia stabilized colloidal silica	*
Solution No. 24	Philadelphia Quartz Co.	Activated silica sol	100
$Na_4P_2O_7$	Fisher Scientific Co.	Anionic electrolyte	100
Calgon C-55	Calgon Corporation	Anionic mixture	75
Calgon 37	Calgon Corporation	Clay-anionic polyelectrolyte mixture	35
Lomar D	Diamond Shamrock Chemical Co. Nopco Chemical Division	Naphthalene sulfonate polymer	19
Primafloc A-10	Rohm and Haas Co.	Anionic polyelectrolyte	15
Purifloc A-21	Dow Chemical Co.	Anionic polyelectrolyte	9
Calgon 240	Calgon Corporation	Anionic polyelectrolyte	5
Poly-Floc 1130	Betz Laboratories, Inc.	Anionic polyelectrolyte	1
M and D Clay	Kentucky-Tennessee Clay Co., Inc.	Ball clay, minus 400 mesh	*
"Red Dog"	Sewickley Township Westmoreland County, Pennsylvania	Similar to (completely burned) coal ash, minus 200 mesh	*
Fly Ash	Colfax Power Station Duquesne Light Co.	Similar to coal ash but not completely burned, minus 400 mesh	500

*Isoelectric point never achieved - remained electropositive

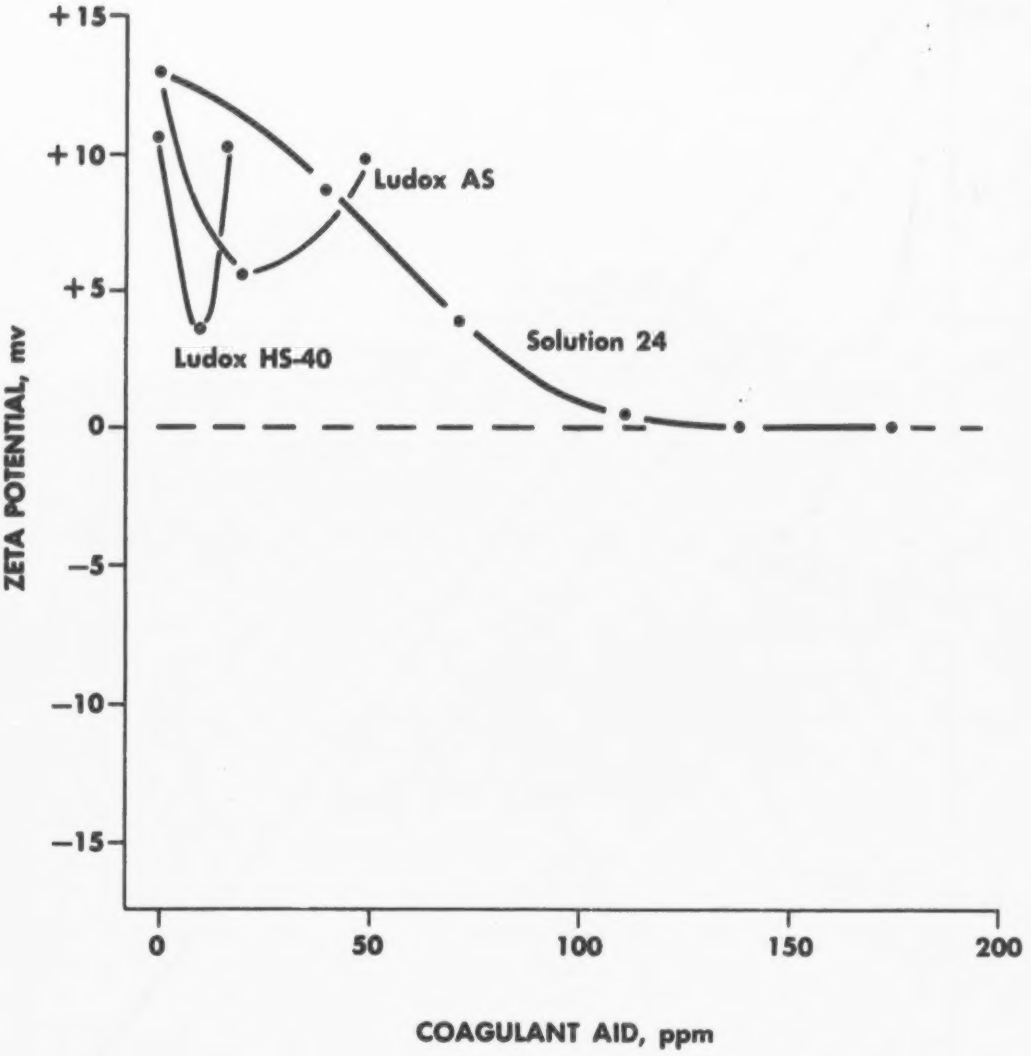

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Figure 18. Effect of Ludox HS-40, Ludox AS, and Solution No. 24 on Zeta Potential of $Fe(OH)_2$

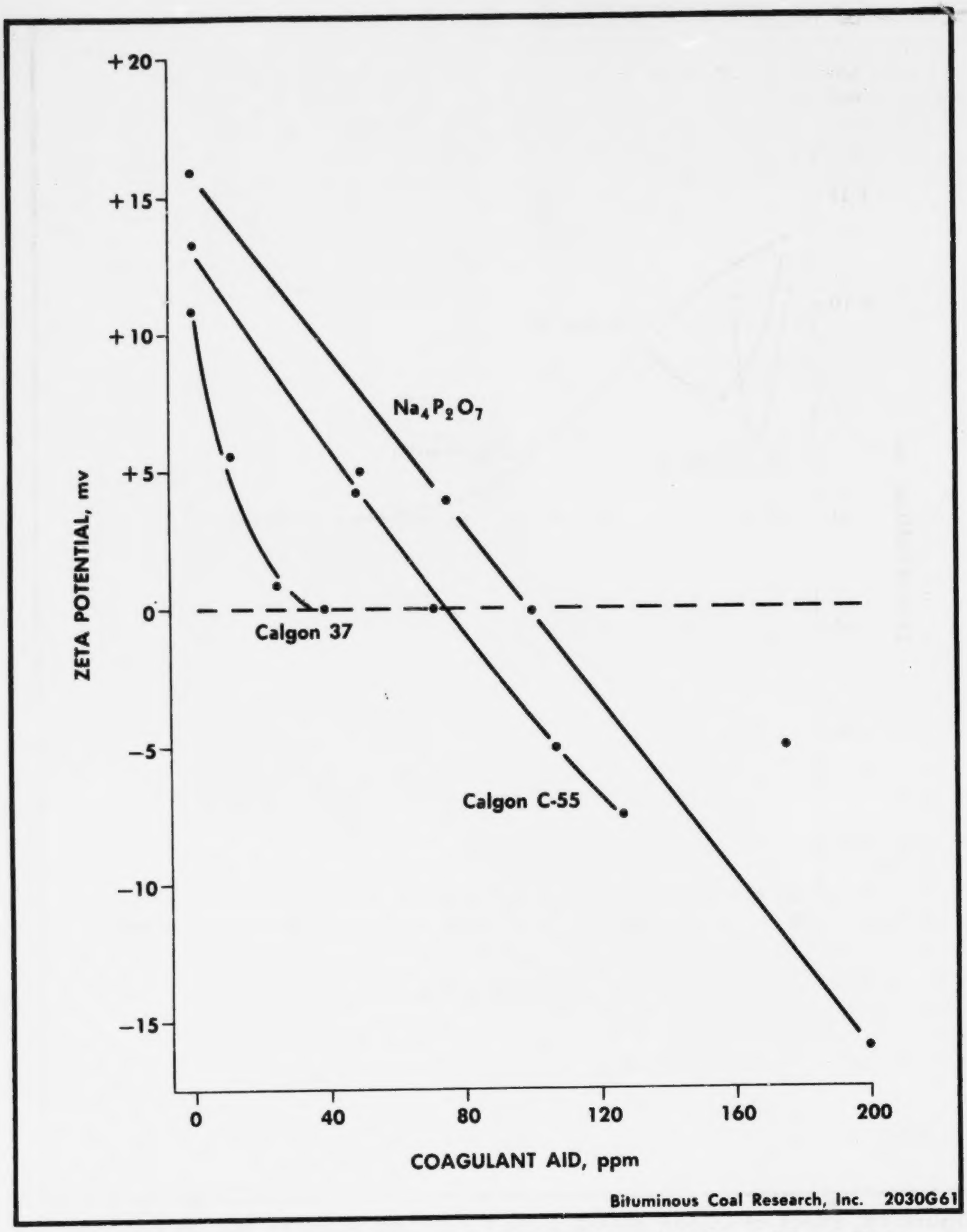

Figure 19. Effect of $Na_4P_2O_7$, Calgon C-55, and Calgon 37 on Zeta Potential of $Fe(OH)_2$

tential from positive to negative. The third curve in Figure 19 shows the effect of Calgon 37, which contains clay as a bulk additive in addition to the anionic polyelectrolyte; the isoelectric point was reached after addition of 35 ppm of the aid.

Figure 20 shows the effect of typical anionic polyelectrolytes as determined in the third set of tests. Efficiency, in terms of the least amount of aid necessary to achieve the isoelectric point, decreased from Calgon 240 through Purifloc A-21 and Primafloc A-10, to Lomar D. The most efficient aid from among all those tested was Calgon 240; approximately 5 ppm was sufficient to achieve the isoelectric point.

Based on the results from the three sets of tests above, Calgon 240 was chosen as the standard to be used in further work. However, a more efficient coagulant aid has since been found, namely Poly-Floc 1130. The isoelectric point was achieved (Figure 21) with only 1 ppm of aid. Other equally efficient coagulant aids are probably available. It is recognized that efficiency must ultimately be determined on the basis of cost per unit of coagulant aid necessary to achieve the isoelectric point.

In the fourth set of tests, the effect of three inert solids, a clay, "red dog", and a fly ash on ferrous hydroxide particles was determined (Figure 22). The isoelectric point was not achieved with up to 1700 ppm of clay, or up to 700 ppm of "red dog." A concentration of approximately 500 ppm of fly ash, however, achieves the isoelectric point, thus indicating that the fly ash is not truly inert. Fly ashes are known to vary considerably in composition and to contain water-soluble material which may be either alkaline or acidic in nature.

Effect of a Combination of Coagulant Aids

To determine the effect of adding both an inert solid and a polyelectrolyte to ferrous hydroxide particles, a single test was made. Figure 23 shows the effect of the addition of fly ash prior to the addition of Calgon 240, both added to ferrous hydroxide suspension. The curve for the addition of Calgon 240 alone to ferrous hydroxide suspension is also included in this figure for comparison. The amount of fly ash used, 500 ppm, was chosen from Figure 22; it was added to the ferrous hydroxide suspension 30 seconds before the addition of Calgon 240. The amount of Calgon 240 necessary to achieve the isoelectric point was reduced by 1 ppm.

Next, the effect of a change in the order of addition of materials was examined. Figure 24 shows the effect of 500 ppm each of fly ash, "red dog", and clay added to the synthetic coal mine water prior to the lime, then the lime, followed in 30 seconds by Calgon 240. The isoelectric point was achieved with fly ash and only 2 ppm of Calgon 240 when they were added in this order.

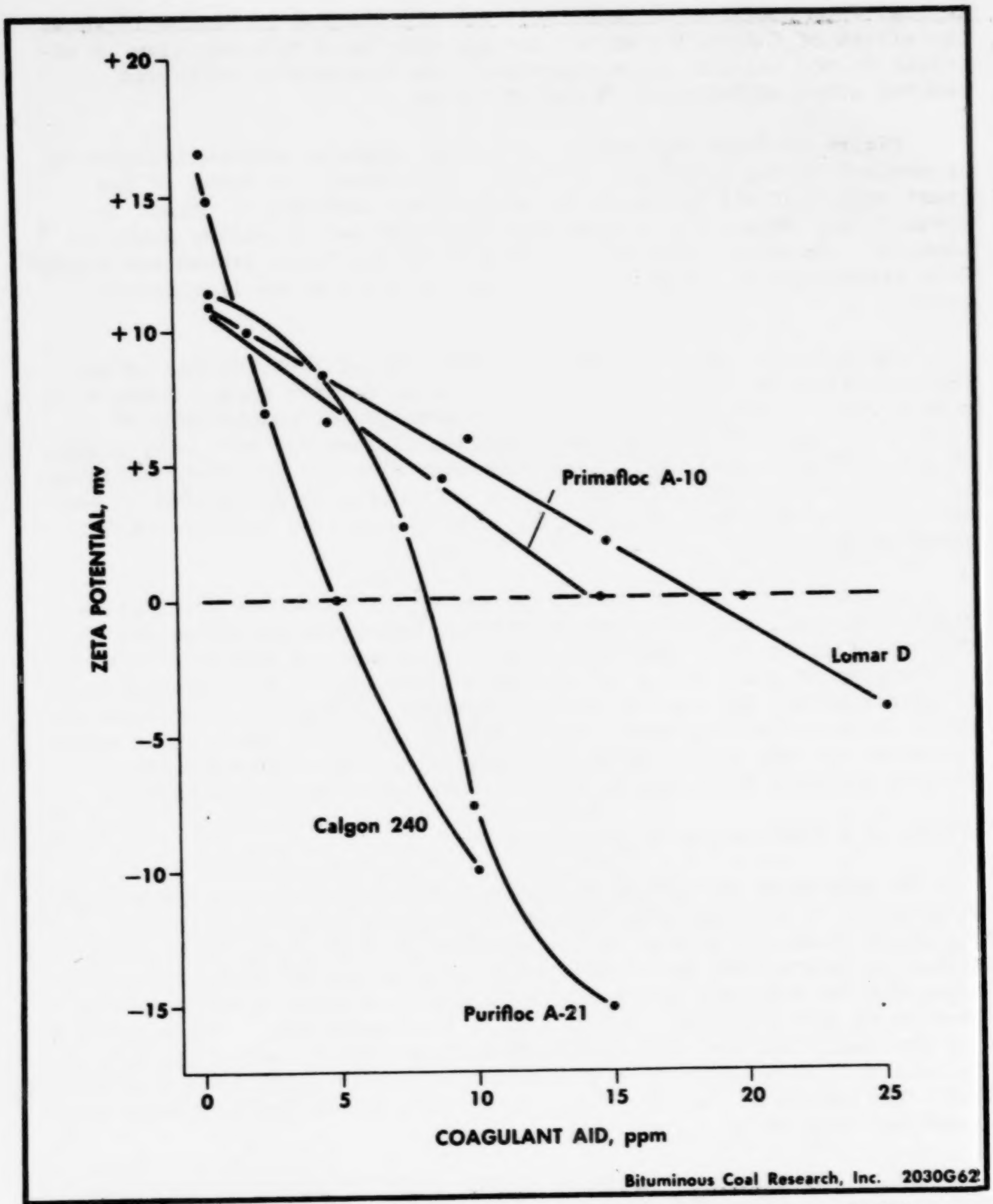

Figure 20. Effect of Lomar D, Primafloc A-10, Purifloc A-21, and Calgon 240 on Zeta Potential of $Fe(OH)_2$

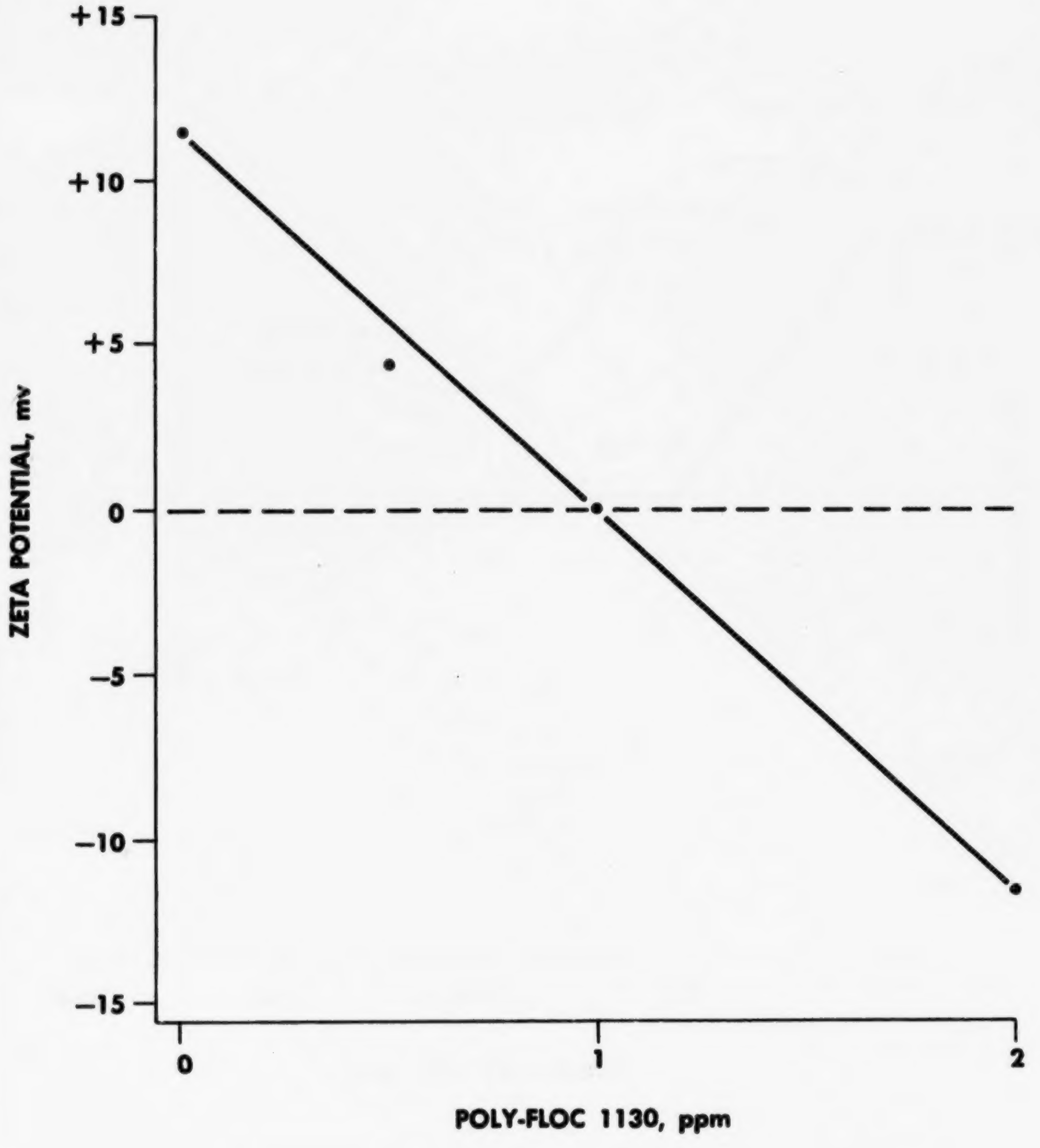

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Figure 21. Effect of Poly-Floc 1130 on Zeta Potential of $Fe(OH)_2$

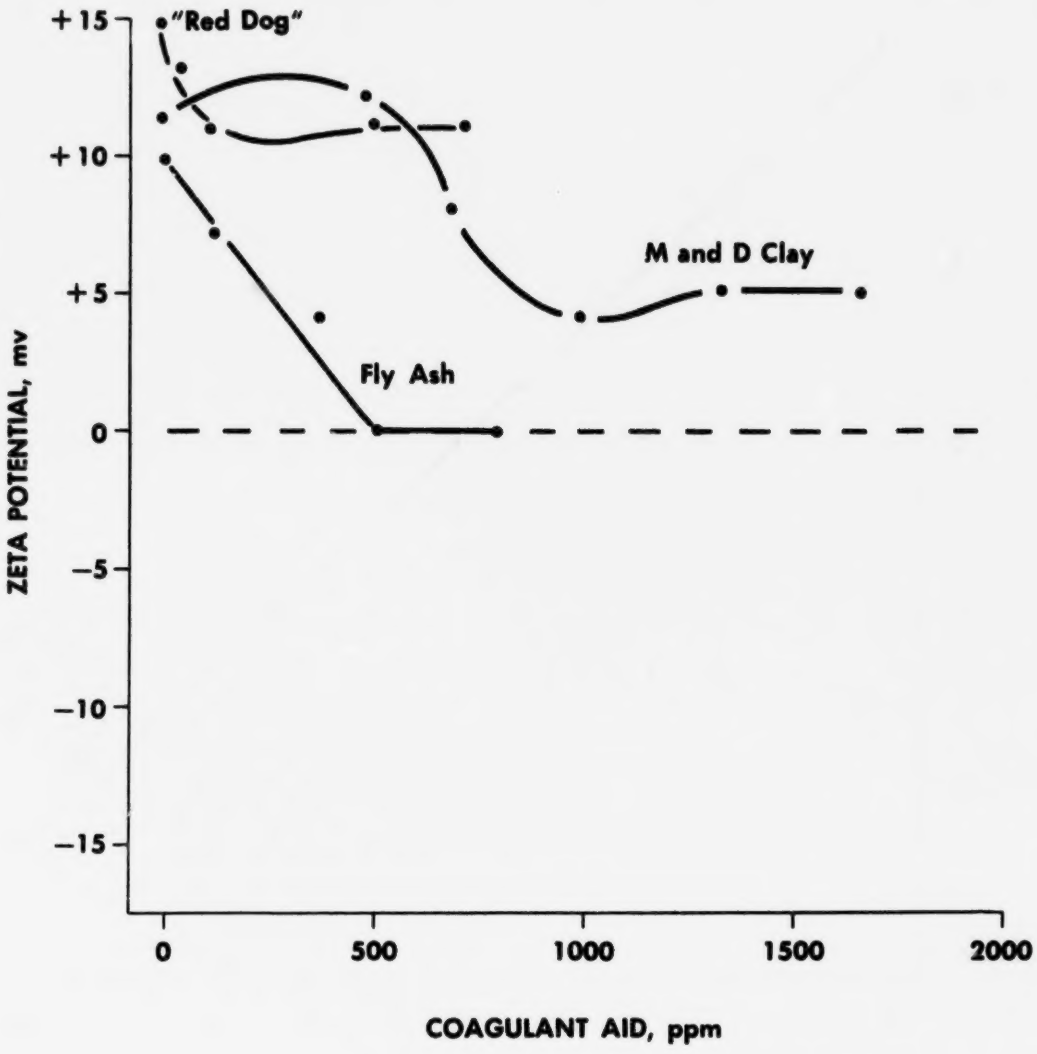

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Figure 22. Effect of M and D Clay, "Red Dog," and Fly Ash on Zeta Potential of $Fe(OH)_2$

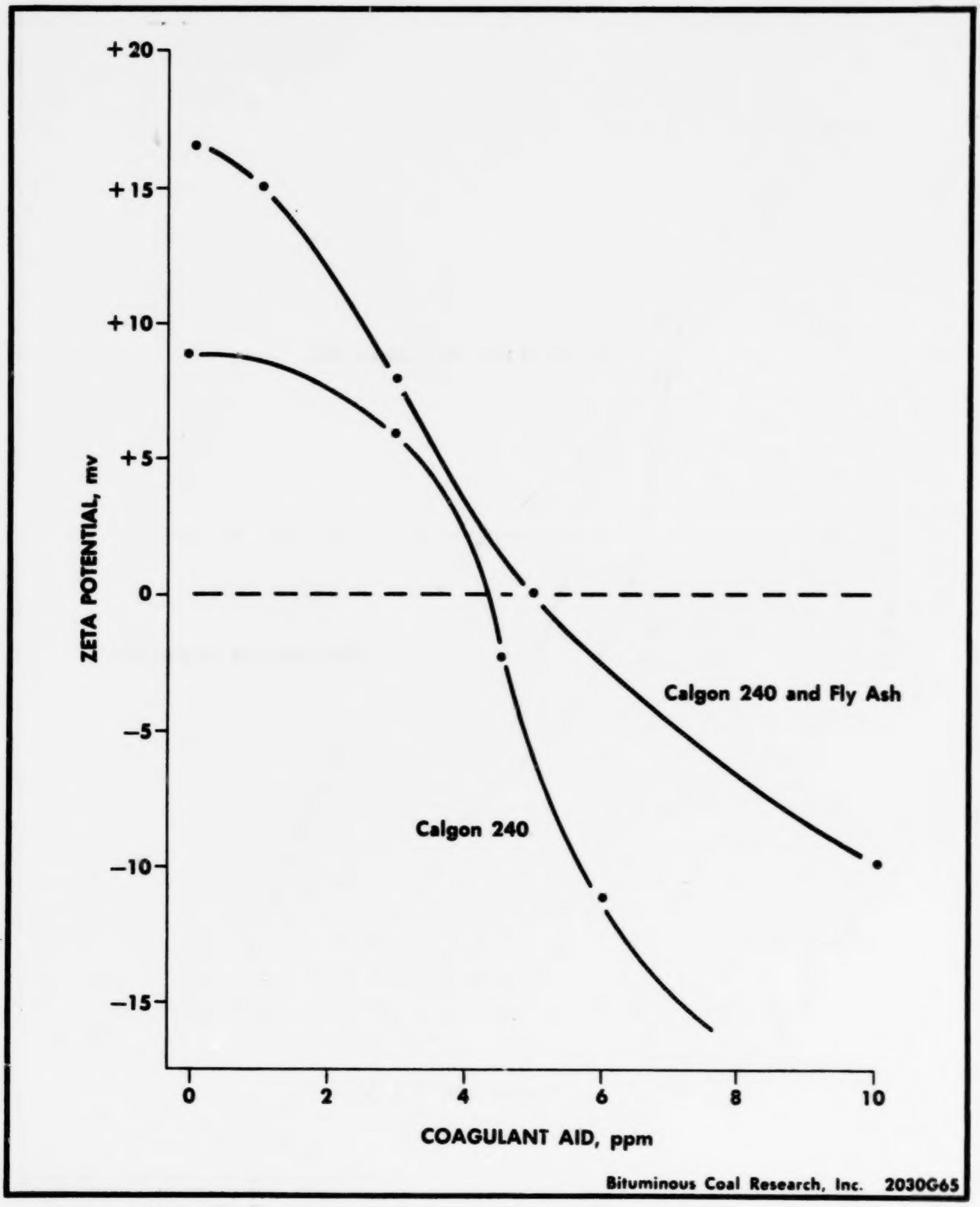

Figure 23. Effect of Calgon 240, and Calgon 240 and Fly Ash on Zeta Potential of $Fe(OH)_2$

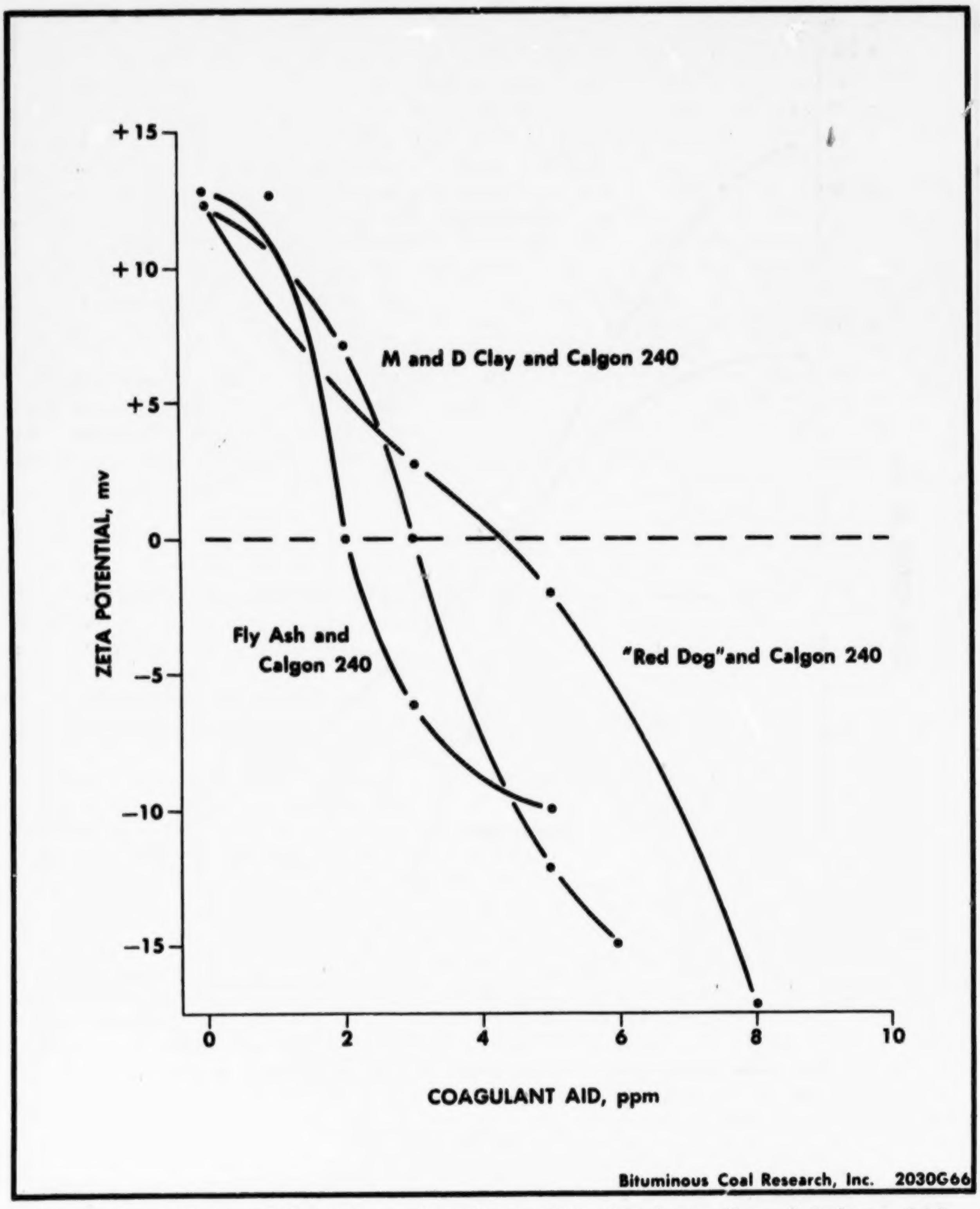

Figure 24. Effect of Fly Ash and Calgon 240, "Red Dog" and Calgon 240, and M and D Clay and Calgon 240 on Zeta Potential of $Fe(OH)_2$

Settling Rate Studies

Finally, the effect of a combination of inert solid and polyelectrolyte on settling rate was studied. Figure 25 shows the settling rate of the sludge without treatment, and the rate with the addition of fly ash followed by lime and then Calgon 240. The use of fly ash-Calgon 240 combination increased the settling rate appreciably; the time required to reach a minimum sludge volume was reduced from about 100 minutes to about 35 minutes. In addition, there was about 25 percent reduction in total sludge volume. Settling of the sludge with clay or "red dog" added together with Calgon 240 was similar to that achieved with fly ash and Calgon 240.

While time did not allow a more comprehensive study of settling rate as affected by coagulant aids, improvement in settling of this particular sludge suggests further examination should be made of these materials as aids in settling sludges produced by any type of coal mine water neutralization.

Magnetic Sludge Studies

In the study of magnetic sludge formation, tests were conducted on both synthetic and actual coal mine waters. Reaction parameters studied were pH, presence of impurities (principally aluminum), temperature, and sludge concentration.

Studies Utilizing Synthetic Coal Mine Water

Initial tests were conducted on a ferrous sulfate solution containing 275 ppm Fe^{2+} and adjusted to pH 3.0 with sulfuric acid. Black magnetic precipitates were obtained readily with either sodium hydroxide or lime added to achieve pH 10.0. However, the products from tests involving NaOH alkalization appeared to be denser, more granular, and exhibited a stronger magnetic response than those resulting from $Ca(OH)_2$ alkalization. When gentle aeration of the alkaline suspension was employed, the rate of conversion to a magnetic product was increased noticeably. For example, with no aeration (stirring only), aeration at 50 ml/min, and aeration at 500 ml/min, magnetic response was observed after 30, 15, and 5 minutes, respectively. Also, as the aeration rate was increased, the increase in Eh toward more oxidizing potentials became quite rapid. The fact that magnetic product was formed in all cases, however, indicates that the magnetic precipitate, once formed, is resistant to further oxidation to $Fe(OH)_3$.

The effect of initial Fe^{2+} concentration on the reaction was also investigated. Three experiments were conducted at initial Fe^{2+} concentrations of 275, 180, and 100 ppm, respectively. Runs were conducted with no aeration (stirring only), aeration at 50 ml/min, and aeration at 500 ml/min at each respective Fe^{2+} concentration level. In all cases, black magnetic products were obtained within 20 minutes; for the runs involving aeration, magnetic response was usually observed within 5 minutes.

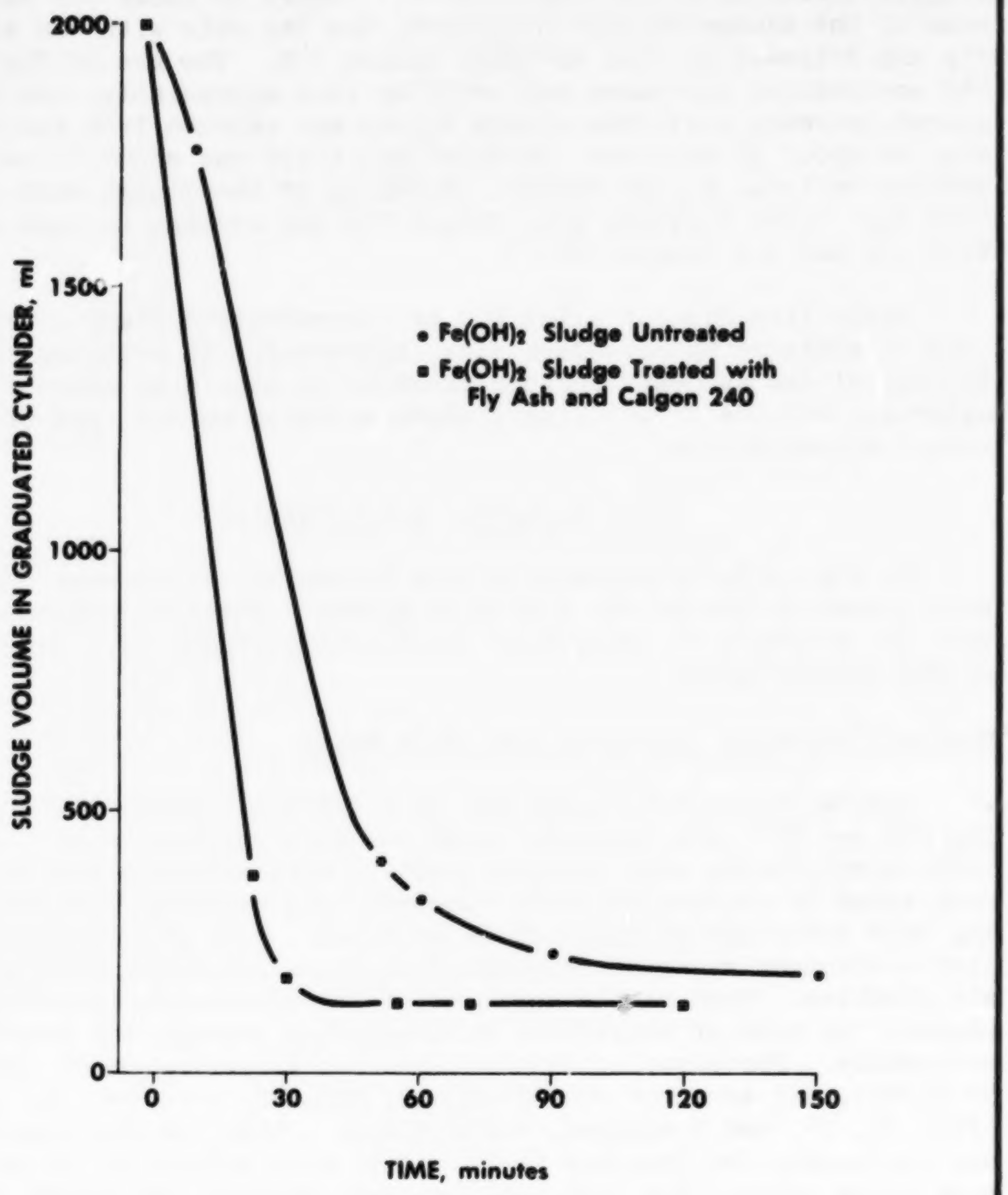

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Figure 25. Effect of Treatment with Fly Ash and Calgon 240 on Settling of $Fe(OH)_2$ Sludge

Studies Utilizing Actual Coal Mine Waters

In contrast to the results with synthetic coal mine water solutions, the results with actual coal mine waters showed considerable variability depending on reaction conditions. Coal mine waters from the Keystone and South Greensburg sites of the Sewickley Creek basin area were chosen for use, because of their characteristically high Fe^{2+}/Fe^{3+} mole ratios, and low aluminum contents.

Early efforts to produce a magnetic product at pH 10.0 were unsuccessful in spite of attempts to promote the conversion, such as: (a) the addition of iron metal powder (0.5 g) to the sample immediately prior to alkalization, (b) the addition of iron metal powder followed by stirring of the sample (at pH 5.0) for 30 minutes prior to alkalization, (c) heating the sample to 75 to 80 C followed by the addition of iron metal powder and NaOH alkalization, and (d) mixing the synthetic coal mine water with the actual coal mine water in the proportions of 2:1, 1:1, and 1:2 actual:synthetic by volume. (The Fe^{2+} concentrations were 175, 200, and 225 ppm for the 2:1, 1:1, and 1:2 mixtures, respectively.)

In a further attempt to promote the conversion to a magnetic precipitate, a portion of a magnetic sludge, previously obtained from lime alkalization of the synthetic coal mine water, was added to a sample of actual South Greensburg coal mine water as seed material. The ultimate reaction product at pH 10.0 was a rust-brown color and exhibited moderate magnetic response. The rather sluggish behavior of the solid in a magnetic field, and its high Fe^{3+}/Fe^{2+} ratio (17.7), indicates that the material may have been a closely consolidated mixture of hydrous ferric oxide and the original magnetic seeding material. Except for this one instance, the ultimate reaction products in all of the tests at pH 10.0 involving actual coal mine water consisted of orange, gelatinous, nonmagnetic solids, presumed to be completely oxidized hydrous ferric oxide.

In later experiments, a pH in the range 8.0 to 8.5 was maintained during the precipitation of iron and the subsequent oxidation reaction, in an effort to minimize interferences due to coprecipitation of magnesium hydroxide which occurs above pH 9.6. A 10 percent lime ($Ca(OH)_2$) slurry was used for neutralization in all of these experiments with actual coal mine waters. In these studies, samples of the ferrous hydroxide suspensions were selected at random and filtered on Whatman No. 42 paper. Results of Fe^{2+} analyses on the filtrates showed that essentially no dissolved iron was present. In addition, no residual dissolved iron was detected in filtrates from the final magnetic sludge suspensions.

With the Keystone coal mine water, which is practically free of dissolved aluminum, precipitated ferrous hydroxide could be readily converted to a dense, black, or dark brown magnetic precipitate near pH 8 provided the following two steps were taken:

The initially formed ferrous hydroxide sludge was first concentrated by gravity settling or centrifugation followed by decantation of the supernatant liquid, and then the thickened sludge was heated to the range 80 to 85 C. Under these same conditions, however, a magnetic product could not be obtained from South Greensburg mine water; the Al/Fe mole ratio in this mine water usually ranges between 0.14 and 0.17. However, if ferrous sulfate was added either to the original coal mine water or to the thickened sludge to decrease the Al/Fe mole ratio to less than 0.12, a magnetic product could be obtained.

Thus, in a typical experiment, ferrous sulfate was added to raw South Greensburg coal mine water to reduce the Al/Fe mole ratio from 0.14 to 0.04 prior to lime addition. In a second experiment using a different sample of mine water from the same source, the Al/Fe mole ratio was reduced from 0.19 to 0.12 in the same manner. In both cases, dark brown magnetic products were obtained after heating the gravity-concentrated sludges to about 80 C for 1.5 hours, with stirring and gentle aeration. In the latter experiment the adjusted Al/Fe mole ratio was confirmed by redissolving a weighed portion of the dried magnetic sludge itself and analyzing the resulting solution by an emission spectrographic technique.

It was observed that the magnetic sludges prepared from South Greensburg coal mine water, after adjustment of the Al/Fe mole ratio with ferrous sulfate, were consistently bulkier, less dense, and lighter in color (various shades of brown) than those prepared from Keystone coal mine water. For example, the total magnetic sludge obtained from a 16-liter sample of Keystone coal mine water settled to a final volume of 87 ml. In both instances, the initial total iron concentration of the raw coal mine water (after addition of ferrous sulfate in the case of the South Greensburg sample) was about 300 ppm. This 3.5-fold difference in sludge volumes must be presumed due, at least in part, to the presence of an appreciable amount of co-precipitated aluminum hydroxide in the South Greensburg coal mine water sludge. In either case, however, conversion of the precipitated ferrous hydroxide sludges to a magnetic form resulted in at least a 5-fold reduction in settled sludge volumes compared to the initial precipitates from lime neutralization.

The use of metallic iron to increase initial Fe^{2+} concentration, thereby decreasing the Al/Fe mole ratio, does not appear promising. For example, in an experiment where South Greensburg coal mine water was stirred with powdered iron for 30 minutes (at pH 5.0 and 23 C), the soluble iron content increased by only 5 ppm.

The effect of impurities on the formation of a magnetic sludge has been adequately demonstrated during these studies. For example, the fact that magnetic sludges were obtained from Keystone coal mine water at pH 8.0 but not at pH 10.0 is probably related to the known inhibiting effect of magnesium hydroxide, which precipitates at pH 9.6.

Furthermore, the fact that the South Greensburg coal mine water sludge could not be converted to a magnetic form until the aluminum/iron mole ratio was reduced to 0.12 or less by the addition of ferrous sulfate, as well as the ease of conversion exhibited by sludges from the aluminum-free Keystone coal mine water, clearly indicate the inhibition due to the presence of aluminum. Interestingly, similar results have been reported by others. Kakabadse and Whinfrey (18) reported that products from the alkalization of mixed ferric sulfate/ferrous sulfate solutions to pH 9.6 were ferromagnetic up to an Al/Fe ratio of 0.026, then became increasingly nonmagnetic, and were completely nonmagnetic above an Al/Fe ratio of 0.105. More recently, Stauffer (19) has found that the magnetic strength of the product, obtained by mixing heated, alkaline suspensions of pure $Fe(OH)_2$ and $Fe(OH)_3$, diminished rapidly when the Al/Fe mole ratio was greater than 0.123, and ferromagnetic properties had essentially vanished when the Al/Fe mole ratio was 0.184. The results of the present study, therefore, are in surprisingly good agreement with those of Stauffer, considering the fact that our results were obtained with actual coal mine water samples where other interferences may have been present.

Of further related interest, Stauffer reported that as the amount of aluminum in the system increased, the reaction product became a lighter brown color and appeared to be more gelatinous in texture. This observation agrees with the results obtained in this study relating to the preparation of a magnetic sludge from South Greensburg coal mine water.

The effect of reaction temperature was quite evident in these studies. At room temperature, the attempted magnetic conversion by aeration of sludge from lime neutralization of Keystone coal mine water was unsuccessful. At 50 C under the same conditions, the sludge exhibited weak magnetic response after 2 hours. This response was transient, however, and oxidation proceeded ultimately to nonmagnetic $Fe(OH)_3$. By contrast, dense, black magnetic sludges were obtained by the time the reaction temperature of 80 C was achieved.

Although the data do not afford a precise explanation of this effect of elevated temperature on ease of magnetic sludge preparation, it is believed to be related to enhanced ordering and possibly renucleation and growth of the magnetic iron oxide crystals at the higher temperatures, as well as dehydration (accelerated aging) processes involving both $Fe(OH)_2$ and $Fe(OH)_3$ prior to their interaction to form the ferrosoferric oxide. Similar processes may be operative as regards coprecipitated calcium sulfate, which is the byproduct of lime neutralization. It is known that insoluble calcium sulfate tends to retard the formation of a magnetic sludge at or near room temperature. In this connection, tests with the Keystone coal mine water sludge at room temperature were never conducted for more than a 6-hour period. Although no magnetic material was ever found within this time interval, the suspended solids characteristically darkened in color from blue-green to dark olive green, indicating some tendency to undergo the desired reaction. After subsequent overnight standing at room temperature, however, these sludges were invariably light brown or orange in color, and nonmagnetic.

As mentioned above, a sludge thickening step was found to be advantageous in the magnetic conversion process. In most instances, gravity settling for about 30 minutes was employed, followed by decantation of the supernatant liquid. Two anionic coagulant aids were found to be effective in reducing sludge settling time without having an adverse effect on its subsequent conversion to a magnetic form. These coagulant aids were Calgon 240 (Calgon Corporation), added to a 4 to 6 ppm level in the sludge suspension, and Poly-Floc 1130 (Betz Laboratories, Inc.), added to a level of 2 ppm.

The effect of further sludge thickening by centrifugation was also investigated. Batch samples of gravity-settled ferrous hydroxide sludges were centrifuged for 10 minutes at 1600 rpm. Centrifugation increased the solids contents from about 2 to 9 percent by weight, a 4.5-fold increase. There was some evidence that this additional solids concentration step resulted in accelerated formation of the magnetic sludge during heating. There were also indications that reductions in final settled sludge volume and increases in solids contents of the magnetic sludge were effected by the centrifugation step. For example, the entire amount of sludge obtained from lime neutralization of 132 liters (35 gallons) of Keystone coal mine water was concentrated by centrifuging to 1 liter. This material was heated to 80-90 C for 2.5 hours; magnetic properties were observed after the first 30 minutes. The magnetic sludge settled overnight to a volume of 230 ml, corresponding to 1.7 ml of sludge per liter of the original coal mine water sample, and had a solids content of 17.7 percent be weight. By comparison, a similar experiment with only gravity-settled solids (also from lime neutralization of Keystone coal mine water) produced a settled magnetic sludge whose volume corresponded to 5.4 ml per liter of coal mine water, and which contained 12.1 percent solids by weight.

On the other hand, centrifuging did not seem to obviate the need for elevated reaction temperatures or reduce the effect of interferences due to cation impurities. Thus, the centrifuged solids from lime neutralization of Keystone coal mine water still could not be converted to a magnetic sludge at room temperature, and magnetic properties did not appear in centrifuged, heated South Greensburg sludges until after the requisite amount of ferrous sulfate had been added.

Finally, it should be pointed out that preliminary sludge thickening by gravity settling and/or centrifugation may not be absolutely essential to the magnetic conversion process. However, if a heating step is required, as the data indicate, it would seem more realistic in terms of a practical coal mine water treatment process to minimize the volume requiring heat treatment. This was the reasoning behind those phases of the experimental work involving preliminary sludge thickening.

Miscellaneous Studies

Effect of Coagulant Aids on $Fe(OH)_3$

Particles of freshly prepared ferric hydroxide formed by limestone neutralization of synthetic coal mine water carry a positive electrostatic charge (+4 to +6 millivolts). Neutralization of this charge should be accomplished by the addition of an anionic polyelectrolyte; if so, coagulation should take place and thus markedly increase the settling rate.

A series of graphs, Figures 26 to 29 inclusive, of zeta potential versus concentration of various coagulant aids was prepared from electrophoretic mobility measurements on ferric hydroxide particles. The amounts of coagulant aids used are listed in Table 24 together with the amounts needed with ferrous hydroxide in studies of non-oxidative neutralization. The amount of coagulant aid required to achieve the isoelectric point with ferric hydroxide is, in general, much less than that required with ferrous hydroxide.

The results are sufficiently encouraging to warrant further study in this area, particularly regarding settling rates.

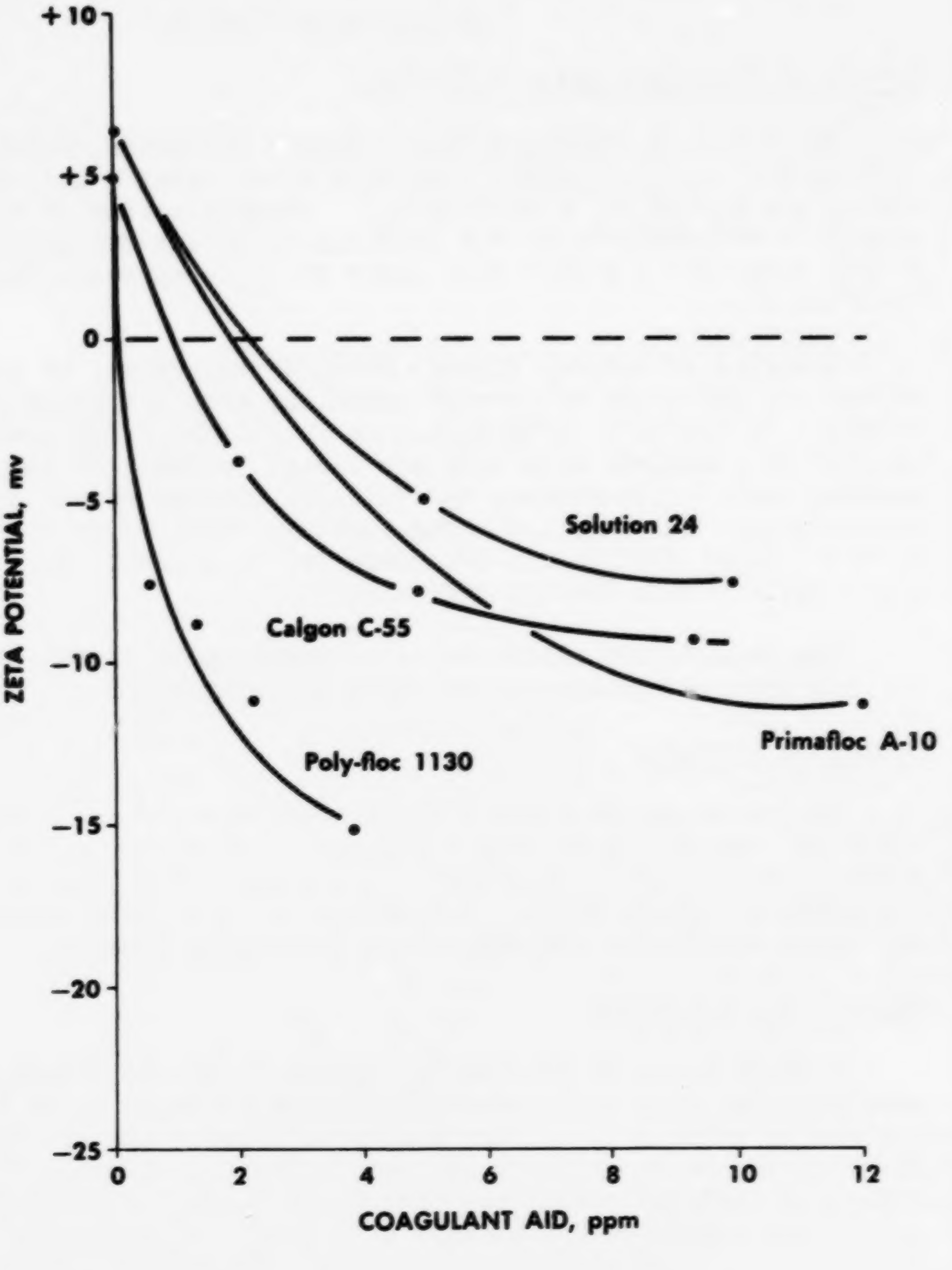
Flotation Studies

Data from six separate flotation experiments are presented in Table 25. In all cases, there was an insignificant separation of froth from tailings. Only when fly ash was added (Test No. 4) was there any material in the froth. The method is completely unsatisfactory under these conditions for separating the sludge from the liquid.

Calcium Ion Electrode

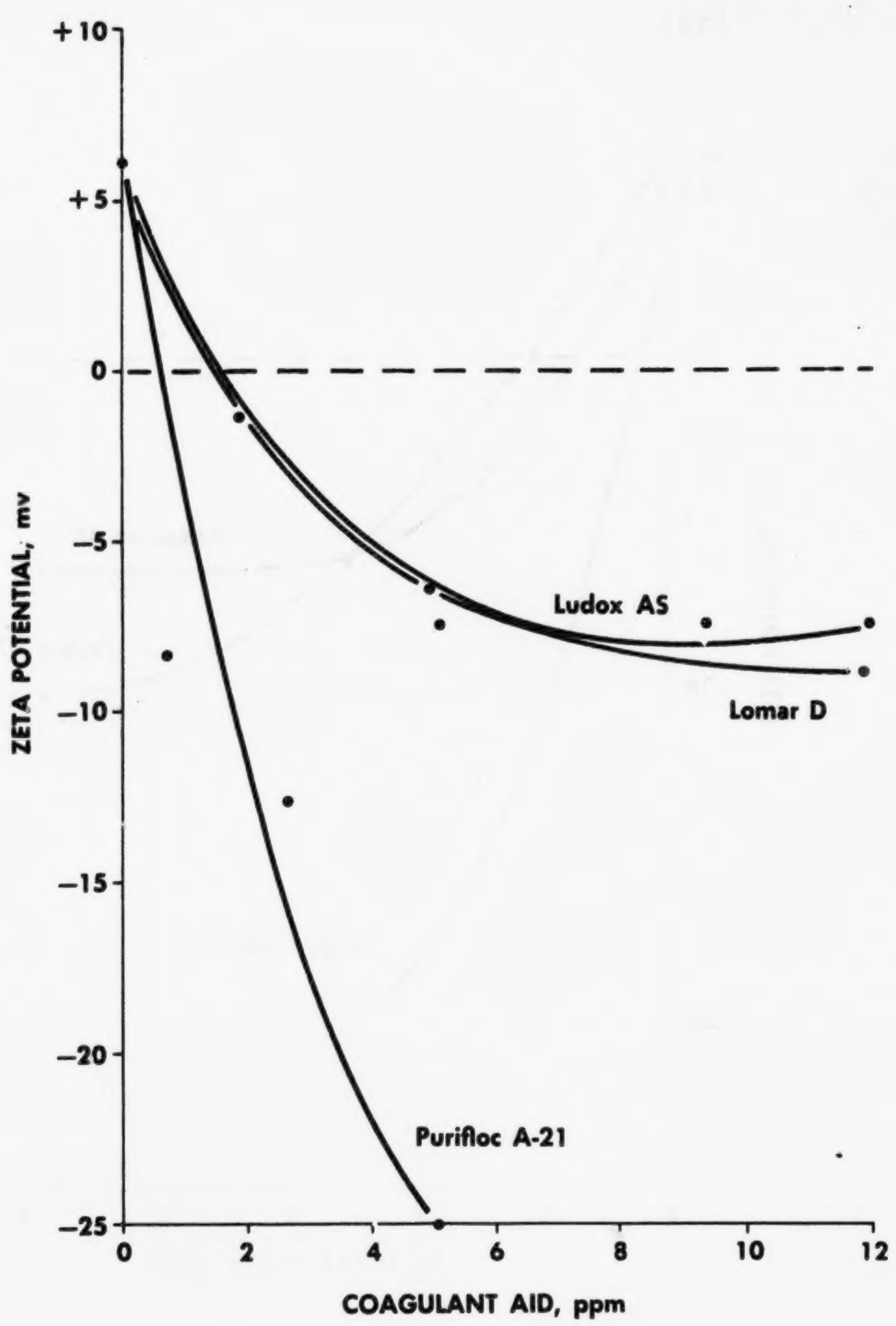
Concentration of calcium ion versus electrode potential plotted on semi-log paper yielded a straight line calibration curve for solutions containing only $CaCl_2$. Introduction of varying amounts of ferrous iron, ferric iron, or aluminum to the same solutions of $CaCl_2$, however, resulted in randomly scattered points, which could not be utilized to obtain the concentration (activity) of Ca^{2+}.

Although the electrode cannot be used to follow the fate of the calcium ion during coal mine water neutralization using lime or limestone, it may still be useful in following the rate of dissolution of limestone in water, in comparing the effect of composition of the stone, particle size, and surface area on solubility, or it may be used to monitor the amount of calcium ion in the effluent after neutralization, if all iron and aluminum are removed.



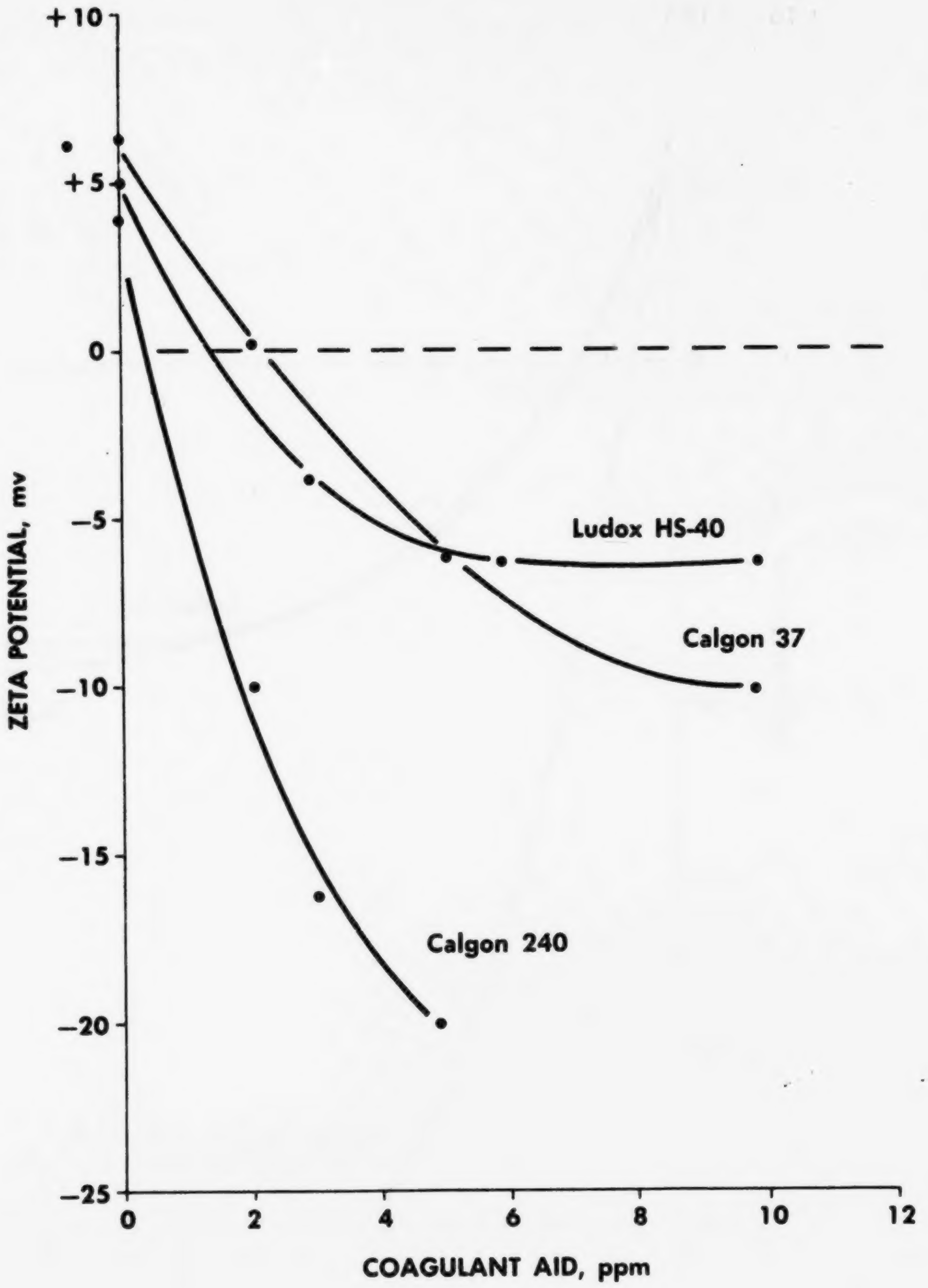
Bituminous Coal Research, Inc. 2030G67

Figure 26. Effect of Poly-Floc 1130, Calgon C-55, Primafloc A-10 and Solution No. 24 on Zeta Potential of $Fe(OH)_3$



Bituminous Coal Research, Inc. 2030G68

Figure 27. Effect of Purifloc A-21, Ludox AS, and Lomar D on Zeta Potential of $Fe(OH)_3$



Bituminous Coal Research, Inc. 2030G69

Figure 28. Effect of Calgon 240, Ludox HS-40, and Calgon 37 on Zeta Potential of $Fe(OH)_3$

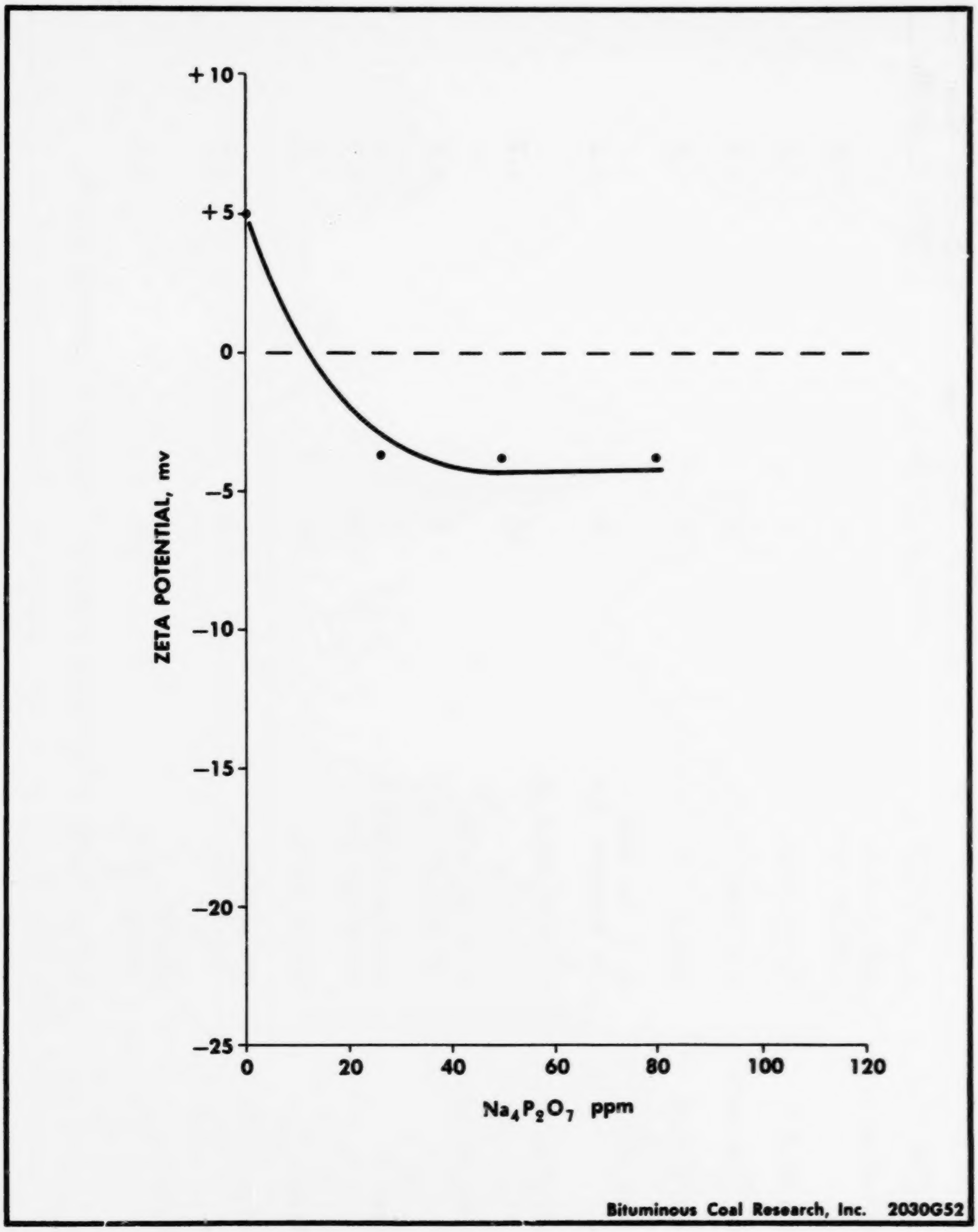


Figure 29. Effect of $Na_4P_2O_7$ on Zeta Potential of $Fe(OH)_3$

TABLE 24. EFFECT OF COAGULANT AIDS ON $Fe(OH)_2$ AND $Fe(OH)_3$

Name	Source	Concentration at Isoelectric Point, ppm Added to $Fe(OH)_2$	Concentration at Isoelectric Point, ppm Added to $Fe(OH)_3$
Poly-Floc 1130	Betz Laboratories, Inc.	1	<0.1
Calgon 240	Calgon Corp.	5	0.4
Purifloc A-21	Dow Chemical Co.	9	0.4
Calgon C-55	Calgon Corp.	75	0.8
Ludox AS	E. I. du Pont de Nemours, Inc.	*	1.1
Primafloc A-10	Rohm and Heas Co.	15	1.2
Ludox HS-40	E. I. du Pont de Nemours, Inc.	*	1.5
Lomar D	Diamond Shamrock Chemical Co.	19	1.5
Calgon 37	Calgon Corp.	35	1.8
Solution 24	Philadelphia Quartz Co.	100	1.8
$Na_4P_2O_7$	(Fisher Scientific)	100	6.0

* Isoelectric point never achieved - remained electropositive.

TABLE 25. FROTH FLOTATION TESTS

Test No.	Volume of Water Treated, ml	Additives	Amount of Additives	Air Flow Rate, cfm	Stirrer Speed, rpm	Froth Time, min	Percent by Weight	
							Froth	Tailings
1	2500	Lime Kerosene Methylisobutyl Carbinol (MIBC)	to pH 8 2 drops 2 drops	1.0	650	1	0.0	100.0
2	2500	Lime MIBC Poly-Floc 1130	to pH 8 2 drops 4 ppm	1.0	650	1	0.0	100.0
3	2500	MIBC Poly-Floc 1130	2 drops 4 ppm	0.5	650	1	0.0	100.0
4	2500	MIBC Poly-Floc 1130, Fly Ash	2 drops 4 ppm 2.5 g	0.5	650	1	13.9	86.1
5	2500	MIBC Lomar D	2 drops 4 ppm	0.5	650	1	0.0	100.0
6	2500	MIBC Arquad 2C-75	2 drops 4 ppm	0.5	1200	1	0.0	100.0

ASTM Activities

No single method or set of conditions for the determination of acidity of coal mine water is utilized by laboratories involved in such determinations, whether the acidity determination is pertinent for a survey of coal mine drainage sources or for neutralization studies. This has resulted in a lack of reproducibility of acidity values on the same mine water as determined by two different laboratories. A lack of understanding of the chemical equilibria involved in this determination has even resulted in different acidity values on a single sample in the same laboratory with two different operators.

Experimental conditions not yet resolved in this determination include: (a) size of sample, (b) internal acid-base indicator versus pH meter for the end point, (c) heating versus boiling the sample, (d) duration of heating or boiling, (e) cooling before titrating versus a hot titration, (f) addition of peroxide (versus no peroxide) to the sample, and (g) the end point itself.

A standardized method for this acidity determination is a necessity for coal mine drainage neutralization, particularly when water quality standards define acidity limits. This, then, is the reason for our involvement in ASTM Committee D-19 on Water--to bring this standardization nearer.

Continuous Flow Tests

The limestone neutralization of the four actual coal mine waters as demonstrated previously in batch-scale neutralizations tests, was studied utilizing the one-gallon-per-minute continuous flow system.

South Greensburg and Keystone

South Greensburg coal mine discharge contained 95 ppm of Fe^{2+} at a pH of 5.1. In a number of experiments using the general procedure, the treated water in the settling tank normally contained 50 ppm of Fe^{2+} at pH 6.5. Aeration for 2 to 3 hours in the settling tanks (using air and a manifold with two gas diffuser stones) reduced this level to about 3 to 10 ppm of Fe^{2+} and increased the pH to 6.6.

In a variation of the general procedure, an experiment was conducted in which aeration was first accomplished in the aeration tank for 100 minutes prior to, instead of after, addition of the limestone. This resulted in a pH of 6.3 and 76 ppm of Fe^{2+} in the settling tank. After further aeration for 1 hour, the concentration of Fe^{2+} was 48 ppm at pH 6.4.

In the next two additional experiments the effect of recirculation of the sludge resulting from the previous treatment of South Greensburg discharge was studied. No attempt was made to concentrate the sludge.

Sludge was added to the water (which had undergone addition of limestone and mixing) in the aeration tank at a rate of one volume of sludge per volume of freshly treated water. This, in effect, reduced the flow rate of freshly treated water from 1.0 gpm to 0.5 gpm. The water in the settling tank contained 52 ppm of Fe^{2+} at pH 6.3. Further aeration for 1 hour in the settling tank resulted in water with 8 ppm of Fe^{2+} at pH 6.4.

In the second experiment studying sludge recirculation, the sludge was added initially to the limestone reactor at a rate equal to the rate of flow of freshly treated water, resulting in a flow of 0.5 gpm of coal mine water actually being treated. The treated water in the settling tank contained only 10 ppm of Fe^{2+} at pH 6.6. Further aeration for 1 hour in the settling tank resulted in water with pH 7.0 and containing 4 ppm of Fe^{2+}.

Keystone coal mine discharge contained 200 ppm of Fe^{2+} at a pH of 6.2. In a typical experiment, treatment of this discharge resulted in a water containing approximately 100 ppm of Fe^{2+} at pH 6.5 in the settling tank. Further aeration in the settling tank for 1 hour reduced the concentration of Fe^{2+} to 20 ppm at pH 6.5.

The effect of recycled sludge was examined in a manner similar to that used with the South Greensburg discharge. In a typical experiment, sludge from a previous neutralization of the Keystone discharge was added to the limestone reactor tank in a volume equal to that of untreated Keystone mine water, resulting in a flow rate of untreated water of 0.5 gpm. Treated water entering the settling tank after aeration now contained only 19 ppm of Fe^{2+} in contrast to 100 ppm in the previous experiments with no sludge recirculation. Further aeration of the water in the settling tank showed a treated water with less than 1 ppm of Fe^{2+} at pH 6.5.

The translation of limestone neutralization of both South Greensburg discharge and Keystone discharge from batch scale to continuous flow was accomplished but with the expected difficulties. Retention times which were sufficient to accomplish nearly complete oxidation of ferrous iron on batch scale were not sufficient using the continuous flow test apparatus. Reduction of iron to a satisfactory level was accomplished in the neutralization of these two waters by sludge recirculation. There was a difference depending on where the sludge was added. Better results were obtained when the sludge was introduced with the untreated mine water in the limestone reactor tank.

Further studies are necessary to establish the minimum volume of sludge necessary to effectively aid in the neutralization (and oxidation) since this affects the rate of flow at which the untreated mine water can be handled in the process.

No claim is made as to the mechansim by which sludge recirculation aids the process. It has been demonstrated, on batch scale only (Figure 13), that greater than twice the stoichiometric amount of limestone does not seem to increase the rate of ferrous iron oxidation. However, the sludge does contain a substantial amount of unreacted limestone in addition to the products which result from the treatment process.

Tarrs

In all of the continuous flow experiments, a comparison is being made with the results of the batch-scale neutralization experiments. (See Discussion Section, Batch-scale Neutralization of Actual Coal Mine Waters.) With the Tarrs discharge this was not possible for the following reasons. At the time of sampling the Tarrs discharge for these continuous flow experiments, the water at the point of discharge contained approximately 40 ppm of Fe^{2+} at pH 3.0, or about half the amount present in the same discharge when sampled for the earlier studies. (See Discussion Section, Batch-scale Neutralization of Actual Coal Mine Waters and Oxidation of Ferrous Iron.) In spite of this reduced concentration of ferrous iron, the studies were conducted with this water as described.

The general procedure was altered by first aerating the water in the aerating tank, pumping this water into the limestone reactor, and then adding limestone. The treated water in the settling tanks typically contained 5 to 20 ppm of Fe^{2+} at pH 5.9. This iron level was attained with aeration either in the presence or absence of activated carbon in the aerating tank. Further aeration for 1 hour, in either case, reduced the concentration of Fe^{2+} to < 1 ppm and increased the pH about 7.

Neutralization of this discharge using the continuous flow system proceeded with little difficulty. Satisfactory oxidation of ferrous iron was accomplished whether the activated carbon was present or not.

It must be stressed again that Tarrs discharge samples for these continuous flow tests contained much less ferrous iron (in fact, much less of all contaminants) than when sampled and used in the batch-scale neutralization experiments. A comparison of batch with continuous flow treatment, therefore, has little meaning since the quality of the water had changed significantly. The reasons for the change in composition of this water should be ascertained. A substitute should be found, if necessary, for this type of coal mine discharge.

Thorn Run

Using the general procedure, treatment of Thorn Run discharge containing 8 ppm of Fe^{2+} at pH 3.0 resulted in water after aeration and entering the settling tank containing 2 ppm of Fe^{2+} at pH 6.4. Further aeration increased the pH to 7.3 and decreased the Fe^{2+} concentration to 1 ppm.

A similar experiment, but with limestone addition, mixing, and aeration all carried out in the limestone reactor tank resulted in a reduction in Fe^{2+} from 23 ppm to 7 ppm and a pH increase from 2.4 to 6.8.

In both cases, aluminum, present originally at a concentration of approximately 50 ppm, was reduced to < 1 ppm.

Treatment of Thorn Run discharge, which contains iron mostly in the ferric state, proceeded with no difficulty. Limestone treatment of this type of coal mine water is most satisfactory.

The results of the continuous flow experiments indicate that neutralization and reduction of iron content can be accomplished by limestone treatment of actual coal mine waters under conditions of flow which simulate actual treatment plant operations. The results, however, show that the treatment conditions must be altered depending on the type of coal mine water.

For example, sludge recirculation was beneficial to the treatment of the South Greensburg and the Keystone discharges in which ferrous iron is the predominant species. In addition, the pH values of these discharges were relatively high, 5.1 for South Greensburg and 6.2 for Keystone.

Use of a catalyst (for example, activated carbon) to aid in the oxidation of ferrous iron in a water having a relatively low pH, such as the Tarrs discharge (at a pH of 3.0) might not only be beneficial but also necessary.

No further steps in the treatment process, such as sludge recirculation or use of a carbon catalyst, were necessary with the Thorn Run discharge. Since this discharge contained only small amounts of iron in the ferrous state but relatively large amounts of both iron in the ferric state (about 60 ppm) and aluminum (about 50 ppm) at a pH of 3.0, the treatment process involved principally neutralization and little or no oxidation.

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